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(54) **MANNOSYLERYTHRITOL LIPID COMPRISING LIQUID RINSE AIDS**

(57) The present invention refers to a rinse aid composition comprising a biosurfactant selected from the group of mannosylerythritol lipids and at least one acidic component, the use of such compositions during automatic dishwashing and methods for cleaning kitchenware and/or tableware in an automatic dishwasher comprising bringing such a composition into contact with said kitchenware and/or tableware during the rinse step.

EP 3 940 049 A1

Description

[0001] The present invention refers to a liquid rinse aid composition comprising a biosurfactant selected from the group of mannosylerythritol lipids, the use of such compositions in an automatic dish washer and methods for cleaning kitchenware and/or tableware in an automatic dishwasher comprising bringing such a composition into contact with said kitchenware and/or tableware during the rinse step.

[0002] Rinse aids are added during the rinsing step of automatic dishwashing programs to prevent droplet formation, so that water drains from the surfaces in thin sheets, rather than forming droplets, which prevents "spotting".

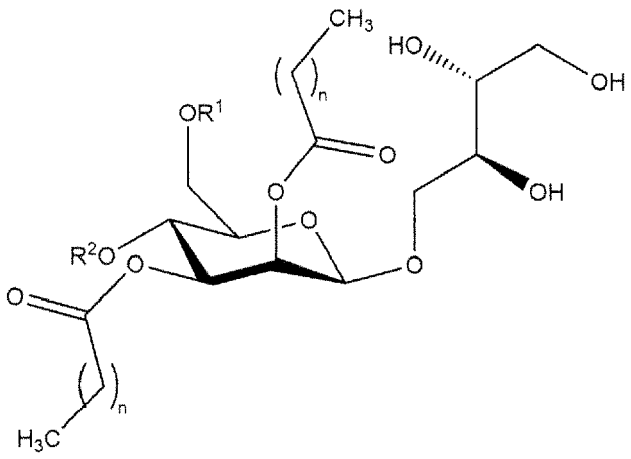
[0003] "Spotting" on washed items is caused by droplets of water drying and leaving behind dissolved limescale minerals, thereby rendering the washed table- or kitchenware less attractive to the consumer. Rinse aids can also improve drying performance as there is less water remaining to be evaporated off the washed items. A thinner sheet of water also has a larger surface-area than a droplet of the same volume, which increases the likelihood of water molecules evaporating. This results in less energy consumption in order to dry the washed items.

[0004] The above-mentioned effects are generally achieved by rinse aids comprising nonionic surfactants. However, conventional rinse aids entirely rely on nonionic surfactants derived from ethoxylated fatty alcohols. Such surfactants are synthesized from petroleum fractions and therefore require high amounts of energy and non-renewable resources during production. Consequently, there is a need for rinse aid compositions being more environmentally friendly and saving recources. It was therefore an object of the present invention to provide a rinse aid composition yielding excellent spotting results, in which at least a part of conventional nonionic surfactants is saved. This object is met by the use of particular, selected surfactants known in the art as biosurfactants.

[0005] Biosurfactants are surfactants which can be produced by biotechnological processes, i.e. using fungi or bacteria, from renewable resources, like sugars and/or oils derived from plants. A further advantage of biosurfactants is that these compounds are readily biodegradable.

[0006] A drawback of the replacement of conventional nonionic surfactants by biosurfactants is a decrease in drying and spotting performance of the resulting rinse aids. However, the present inventors have surprisingly found that drying and spotting performance of rinse aid compositions comprising biosurfactants can be improved by incorporating mannosylerythritol lipids into such rinse aid compositions.

[0007] Mannosylerythritol lipids are molecules having the general formula (I) below.



Formula (I)

[0008] Depending on the degree of acetylation, mannosylerythritol lipids are divided into subtypes called MEL-A (R^1 = R^2 = Ac), MEL-B (R^1 = Ac, R^2 = H), MEL-C (R^1 = H, R^2 = Ac) and MEL-D (R^1 = R^2 = H), wherein Ac is the abbreviation for an acetyl residue.

[0009] Within the context of the present invention, for all subtypes n may be an integer having a value between 1 and 24, preferably between 2 and 18, more preferred between 4 and 12 and between 14 and 18, most preferred 3, 4, 5, 9, 10, 11, 15, 16 or 17.

[0010] Such biosurfactants are typically produced using bacteria of the species Pseudozyma or Ustilago.

[0011] Mannosylerythritol lipids have previously been described as used in cleaning compositions. WO 2018/197623 A1, WO 2015/091250 A1 and WO 2018/191174 A1 describe compositions comprising biosurfactants useful for cleaning hard and/or soft surfaces. EP 3 290 020 A1 and US 2010/168405 A relate to the use of mannosylerythritol lipids in medicinal or cosmetic compositions, while WO 2016/066464 A1, EP 3 341 458 A1, EP 3 290 500 A1, DE 10 2015 217 506 A1 and DE 10 2014 225 184 A1 refer to mannosylerythritol lipid containing detergents, particularly laundry detergents.

[0012] Mannosylerythritol lipids may also be used as thickeners or corrosion inhibitors, as disclosed in WO 2018/167285

A1 and EP 2 872 480 A1, or WO 2018/095975 A1, respectively.

[0013] However, none of the above-mentioned prior art documents teaches beneficial properties of mannosylerythritol lipids when incorporated into a rinse aid composition.

[0014] In case within this disclosure the rinse aid composition according to the present invention is defined as being free of a specific component, "free" in this context means that, despite efforts taken to avoid the presence of said component in the rinse aid composition, a total amount of not more than 10 ppm, preferably not more than 5 ppm, more preferred not more than 2 ppm of said component may be present in the rinse aid composition according to the present invention. Most preferred the inventive rinse aid composition contains less than 1 ppm, or 0 ppm of any undesired components.

[0015] Amounts given within here are presented in wt.-% based on the total weight of the inventive rinse aid composition, unless otherwise stated.

BIOSURFACTANTS

[0016] The rinse aid composition according to the present invention comprises at least one biosurfactant selected from the group of mannosylerythritol lipids. Said biosurfactant(s) may be of any of the subtypes MEL-A to MEL-D as defined in Formula (I) above or a mixture of mannosylerythritol lipids of said subtypes. This means that of the two hydroxy groups present in the at least one biosurfactant, 0 to 2 may be acetylated and n may be an integer having value between 1 and 24, preferably between 2 and 18, more preferred between 4 and 12 and between 14 and 18, most preferred 3, 4, 5, 9, 10, 11, 15, 16 or 17.

[0017] The above-defined biosurfactant(s) may be present in the rinse aid composition in a total amount of from 1 to 15 wt.-%, preferably from 3 to 12 wt.-%, more preferred from 5 to 10 wt.-%, based on the total weight of the rinse aid composition.

ADDITIONAL NONIONIC SURFACTANTS

[0018] The rinse aid composition may preferably additionally comprise at least one further nonionic surfactant different from mannosylerythritol lipids.

[0019] Preferred nonionic surfactants different from mannosylerythritol lipids are alkoxylated fatty alcohols, alkoxylated fatty acids or combinations thereof. The relative hydrophilic alkoxy-chain may comprise or essentially consist of ethylene oxide, propylene oxide or butylene oxide or combinations thereof.

[0020] The length of this alkoxy-chain can vary between averagely 1 and averagely 200 (total) ethylene oxide-, propylene oxide- or butylene oxide-groups or combinations thereof, including 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 and the ranges between the particularly mentioned. The relative hydrophobic hydrocarbon-chain from the fatty alcohol or fatty acid can be saturated, monounsaturated or poly-unsaturated and linear or branched. The length of this hydrocarbon-chain may vary between 4 and 30 carbon molecules, including 6, 8, 10, 11, 12, 14, 16, 18, 20, 5 22, 24, 26 or 28.

[0021] Preferred surfactants of this type may be represented by the formula $R^1O(CH_2CH_2O)_x(CH(CH_3)CH_2O)_yH$, wherein R^1 is a linear or branched, saturated or unsaturated hydrocarbon residue having 4 to 30 C atoms, preferably 6 to 26, even more preferred 10 to 24 carbon atoms, x preferably is an integer of from 8 to 200, preferably from 20 or from 25 to 200, y preferably is an integer of at most 100 and x+y is preferably below 200.

[0022] Particularly preferred are alcohol ethoxylates that can be prepared by ethoxylation of a fatty chain alcohol. The preferred alcohol ethoxylates have a hydrocarbon-chain that ranges from 4 up to 26 carbon atoms, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 20 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups. Also preferred are fatty acid ethoxylates that can be prepared by a reaction of fatty acid with ethylene oxide or a polyglycol with the general formula $RCOO-(CH_2CH_2O)_nH$. When a polyglycol is used a mixture of mono- and di-esters ($RCOO-(CH_2CH_2O)_n-OCOR$) is produced. The preferred fatty acid has a hydrocarbon-chain R that varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22. The number of ethylene oxide-groups in the fatty acid ethoxylate is between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups.

[0023] Such additional nonionic surfactants may be any nonionic surfactant known in the art with the exception sorbitan esters, i.e. mono-, di- or triesters of sorbitol and fatty acids, which the composition is free of. If present, additional nonionic surfactants are most preferably selected from ethoxylated alcohols.

[0024] Ethoxylated alcohols may be selected from the group of C_8-C_{20} ethoxylated alcohols, preferably from the group of C_8-C_{10} and C_{16}-C_{18} ethoxylated alcohols.

[0025] Commercially available mixtures of ethoxylated alcohols comprise for example those sold under the trade names of Plurafac® and Emulan® by BASF.

[0026] If such additional nonionic surfactants are present, such nonionic surfactants may be present in the rinse aid composition in a total amount of from 0.1 to 10 wt.-%, preferably from 0.3 to 6 wt.-%, more preferred from 0.5 to 4 wt.-

%, most preferred from 0.7 to 2 wt.-% based on the total weight of the rinse aid composition.

[0027] Consequently, if applicable, the ratio of the total amount of biosurfactant(s) to the total amount of other nonionic surfactant(s) may be between 20:1 and 1:1, preferably between 10:1 and 3:1, more preferred between 8:1 and 5:1.

ACIDIC COMPONENT

[0028] The rinse aid composition according to the present invention highly preferred comprises an acidic component and preferably has an acidic pH value, i.e. the pH of the rinse aid composition is preferably below 7. An acidic pH value is beneficial in order to avoid precipitation of magnesium and/or calcium hydroxides from the rinsing liquor. If precipitated, these salts would then become deposited in form of a cloudy or milky film on the washed dishware, which is considered as an improper cleaning result by the consumer.

[0029] Such an acidic component may be an organic or inorganic, mono- or polyprotic acid, and/or an anionic surfactant containing phosphoric acid mono- and/or diester groups.

[0030] Organic or inorganic acids may be selected from any water-soluble organic or inorganic acids, preferably selected from the group consisting of phosphoric acid, sulfuric acid, hydrochloric acid, boric acid, lactic acid, citric acid, formic acid, acetic acid, glycolic acid, succinic acid, adipic acid, malic acid, maleic acid, gluconic acid and tartaric acid.

[0031] Anionic surfactants containing phosphoric acid mono- and/or diester groups are preferably selected from ethoxylated alkyl phosphates and/or ethoxylated alkyl aryl phosphates.

[0032] Preferred alkyl phosphates and alkyl ether phosphates can be prepared by treating fatty alcohols or (fatty) alcohol ethoxylates with a phosphorylating agent which yields in a mixture of mono- and di-esters of phosphoric acid.

[0033] Preferably, the acidic component is selected from phosphoric acid and/or ethoxylated alkyl phosphates and such phosphates are preferably selected from C_8-C_{20} ethoxylated alkyl phosphates, more preferred C_8-C_{16} ethoxylated alkyl phosphates, even more preferred C_8-C_{14} ethoxylated alkyl phosphates, most preferred C_8-C_{10} ethoxylated alkyl phosphates, wherein preferably ethoxylated alkyl phosphates contain 3 to 10 ethylene oxide repeating units (EO), more preferred 4 to 8 EO, even more preferred 4 to 6 EO and most preferred 5 EO.

[0034] Such anionic surfactants are commercially available, for example under the trade name of Servoxyl® by KLK OLEO.

[0035] Acidic components as defined above may be present in the rinse aid composition in a total amount of from 0.1 to 10 wt.-%, preferably from 0.5 to 5 wt.-%, more preferred from 1 to 3 wt.-%, based on the total weight of the rinse aid composition.

SOLVENTS

[0036] The rinse aid composition according to the present invention is a liquid rinse aid composition. It may therefore comprise 50 to 98 wt.-%, preferably 75 to 95 wt.-%, more preferred 80 to 90 wt.-%, based on the total weight of the rinse aid composition, of a solvent or a mixture of solvents.

[0037] This enables the rinse aid composition to become readily dissolved in the rinsing liquor, thereby avoiding redeposition of any undissolved components from the rinse aid composition on washed items.

[0038] The solvent or mixture of solvents may comprise one or more solvents selected from water, ethanol, 2-propanol and/or glycerol and preferably comprises water.

ENZYMES

[0039] A skilled person will acknowledge that biosurfactants are more prone to enzymatic degradation than conventional surfactants. Therefore, in order to avoid such degradation of biosurfactants by cleavage of ester or ether bonds, it is therefore particularly preferred that the rinse aid composition according to the present invention is free of enzymes cleaving such bonds.

[0040] Free in this context means that, despite efforts taken to avoid the presence of enzymes in the rinse aid composition, a total amount of not more than 1 ppm of ester or ether cleaving enzymes may be present in the rinse aid composition according to the present invention.

MISCELLANEOUS INGEDIENTS

[0041] The rinse aid composition according to the present invention may additionally to the above-mentioned components comprise any ingredients known by a skilled person useful in a rinse aid composition. Such components may for example be complexing or sequestering agents, salts or corrosion inhibitors.

[0042] Preferred salts are water-soluble salts of magnesium, zinc and/or bismuth, as these ions are able to suppress glass corrosion occurring from excess chelating agents, which may present in the rinsing liquor for example due to low

water hardness of the used rinsing water.

[0043] In a preferred embodiment, the rinse aid composition contains a mixture of: biosurfactants selected from mannosylerythritol lipids, ethoxylated fatty alcohols, in particular those selected from C_8-C_{10} and C_{16}-C_{18} ethoxylated fatty alcohols, acidic components, in particular those selected from C_8-C_{10} ethoxylated alkyl phosphates and phosphoric acid and water. In a particularly preferred embodiment, the rinse aid composition consists of these components.

PROPERTIES

[0044] The inventive rinse aid composition may have a pH value of from 1.5 to 4, preferably from 2 to 3. It may have a density from 1.00 to 1.30, preferably 1.00 to 1.15, more preferably 1.00 to 1.05.

EXAMPLE

[0045] All tested rinse aid compositions contained 7.5 wt-% of the respective biosurfactant, 1 wt.-% of nonionic surfactant C_{16}-C_{18} alcohols, ethoxylated, 1.9 wt.-% of acidic components (C_8-C_{10} ethoxylated fatty alcohol phosphates) and ad 100 wt.-% water and had an acidic pH value.

[0046] Biosurfactants tested were two rhamnolipid-based biosurfactants, namely Raphynal V1 200 (abbreviated as RL 1), and a mixture of approx. 65 to70 % diramnolipids and approx. 15 to 20 % mono-ramnolipids (abbreviated as RL 2), one sophorolipid-based biosurfactant, namely Rewoferm® SL One (ex Evonik) (abbreviated as RL 3) and mannosylerythritol lipids as described herein (a mixture of lipids having in formula (I) values for n of 4, 10 and 16; inventive example, abbreviated as MEL).

[0047] Dishes were washed in a Miele GSL-2 dishwasher over 6 cycles in the standard program at 50 °C (rinsing time 8 minutes). The water hardness was 9 °GH.

[0048] Dishes used were eight glasses (goblet-formed, cola and longdrink glasses), six plastic dishes of different materials (melamine-based, polypropylene-based and styrene-acrylonitrile-based), four steel knives and six black ceramic dishes.

[0049] Dishes were checked for droplets and spotting after 4, 5 and 6 cycles, respectively. The number of droplets were determined 30 minutes after finishing the respective number of cycles, while spotting was determined 3 hours after finishing the respective number of cycles, both by visual inspection of an experienced person.

[0050] Drying performance was rated on a scale of 0 to 10, wherein 0 stands for no droplets remaining on the respective dishes and wherein 10 stands for a high number of droplets.

[0051] Spotting performance was rated on a scale ranging from 1 to 7, wherein 1 stands for a high number of spots on the respective dishes and 7 stands for no spots.

[0052] Results are shown in Figures 1 and 2. The values are given as average values over 4, 5 and 6 cycles for all dishes of the same respective material and as average values for all dishes over 4, 5 and 6 cycles (right column).

[0053] It becomes clear from these figures that an inventive rinse aid composition comprising mannosylerythritol lipids as biosurfactants shows better average drying and spotting performance over all tested dishes than rinse aids containing other biosurfactants.

Claims

1. A rinse aid composition comprising:

   at least one biosurfactant selected from the group of mannosylerythritol lipids; and
   at least one acidic component;
   wherein the rinse aid composition is free of ingredients selected from enzymes and/or sorbitan esters.

2. The rinse aid composition according to claim 1, wherein the mannosylerythritol lipid(s) is/are present in a total amount from 1 to 15 wt.-%, preferably from 3 to 12 wt.-%, more preferred from 5 to 10 wt.-%, based on the total weight of the rinse aid composition.

3. The rinse aid composition according to any preceding claim further comprising at least one further nonionic surfactant different from mannosylerythritol lipids.

4. The rinse aid composition according to claim 3, wherein the further nonionic surfactant(s) is/are selected from ethoxylated alcohols.

5. The rinse aid composition according to claims 3-4, wherein the further nonionic surfactant(s) is/are selected from the group of C_8-C_{20} ethoxylated alcohols, preferably selected from the group of C_8-C_{10} and C_{16}-C_{18} ethoxylated alcohols.

6. The rinse aid composition according to claims 3-5, wherein the further nonionic surfactant(s) is/are present in a total amount of from 0.1 to 10 wt.-%, preferably between 0.3 to 6 wt.-%, more preferred from 0.5 to 4 wt.-%, most preferred from 0.7 to 2 wt.-% based on the total weight of the rinse aid composition.

7. The rinse aid composition according to claims 3-6, wherein the ratio of the total amount of biosurfactant(s) to the total amount of further nonionic surfactant(s) is of from 20:1 to 1:1, preferably from 10:1 to 3:1, more preferred from 8:1 to 5:1.

8. The rinse aid composition according to any preceding claim,
wherein the acidic component(s) is/are selected from

(I) the group containing phosphoric acid, sulfuric acid, hydrochloric acid, boric acid, lactic acid, citric acid, formic acid, acetic acid, glycolic acid, succinic acid, adipic acid, malic acid, maleic acid, gluconic acid and tartaric acid; and/or
(II) anionic surfactants containing phosphoric acid mono- and/or diester groups.

9. The rinse aid composition according to claim 8, wherein anionic surfactants are selected from ethoxylated alkyl phosphates and/or ethoxylated alkyl aryl phosphates.

10. The rinse aid composition according to claims 8-9, wherein the acidic component(s) is/are selected from phosphoric acid and/or ethoxylated alkyl phosphates, wherein ethoxylated alkyl phosphates are selected from C_8-C_{20} ethoxylated alkyl phosphates, preferably C_8-C_{16} ethoxylated alkyl phosphates, more preferred C_8-C_{14} ethoxylated alkyl phosphates, most preferred C_8-C_{10} ethoxylated alkyl phosphates.

11. The rinse aid composition according to any preceding claim,
wherein the acidic component(s) is/are present in a total amount of from 0.1 to 10 wt.-%, preferably from 0.5 to 5 wt.-%, more preferred from 1 to 3 wt.-%, based on the total weight of the rinse aid composition.

12. The rinse aid composition according to any preceding claim being a liquid rinse aid composition comprising 50 to 98 wt.-%, preferably 75 to 95 wt.-%, more preferred 80 to 90 wt.-%, based on the total weight of the rinse aid composition, of a solvent or a mixture of solvents.

13. The rinse aid composition according to claim 12, wherein the solvent or mixture of solvents comprises one or more solvents selected from water, ethanol, 2-propanol and/or glycerol, preferably water.

14. Use of the composition according to any preceding claim as a rinse aid in an automatic dishwasher.

15. A method of cleaning kitchenware and/or tableware in an automatic dishwasher comprising adding a composition according to claims 1-13 in the rinsing step.

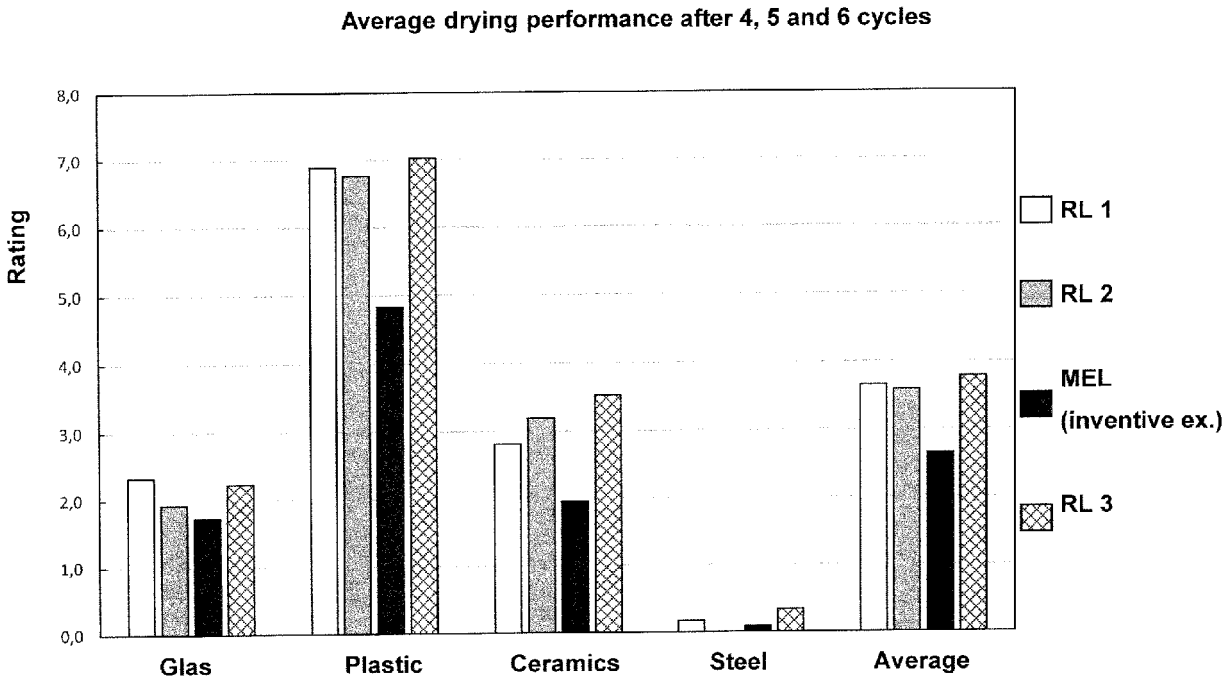


Figure 1: Drying performance (lower values are better)

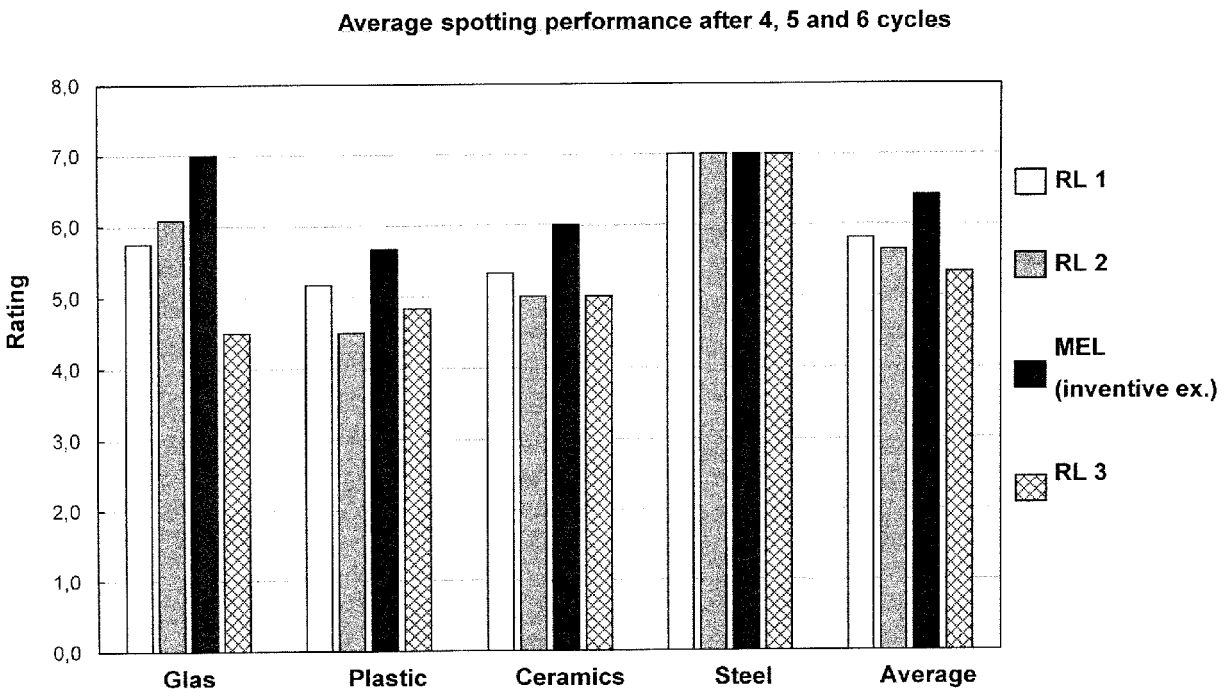


Figure 2: Spotting performance (1 = high spotting, 7 = no spots)

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EUROPEAN SEARCH REPORT

Application Number
EP 20 18 5460

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	WO 2019/214968 A1 (BASF SE [DE]) 14 November 2019 (2019-11-14) * page 16, line 16 - line 18 * * page 18, line 1 - line 35 * * page 23, lines 7-15, 36 - page 24, line 4 * * claims 1, 6-10, 15 * * page 26, line 2 - line 15 * -----	1-15	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	1 December 2020	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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01-12-2020

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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