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(71) Applicants:
- **Becker, Bernhard**
  67294 Oberwiesen (DE)
- **Becker, Hermann**
  67304 Steinborn (DE)
- **Becker, Peter Philipp**
  76889 Klingenmünster (DE)

(72) Inventor: **BECKER, Peter Philipp**
76889 Klingenmünster (DE)

(74) Representative: **Best, Michael et al**
Lederer & Keller
Patentanwälte Partnerschaft mbB
Unsöldstrasse 2
80538 München (DE)

(54) **Process for cleaning a surface of a vehicle**

(57) The present invention relates to a process for cleaning a surface of a vehicle comprising providing an oxalic acid containing cleaning concentrate, diluting the cleaning concentrate to obtain a cleaning composition and applying the cleaning composition to the surface of the vehicle. The cleaning concentrate contains at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerine and at least 11 wt.-% of oxalic acid, wherein wt.-% is based on the total weight of the cleaning concentrate. The cleaning concentrate is stable against precipitation despite its high oxalic acid content.

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Description

[0001] The present invention relates to a process for cleaning a surface of a vehicle. The process comprises providing an oxalic acid containing cleaning concentrate, diluting the cleaning concentrate to obtain a cleaning composition and applying the cleaning composition to the surface of the vehicle.

[0002] Cleaners are used in very different fields which all have specific requirements for the cleaner and the method of cleaning. The choice of the cleaner and method of cleaning e.g. depend on the characteristics of the object to be cleaned and the soil which contaminates the object and which should be removed by cleaning. Depending on the object to be cleaned and the circumstances of cleaning, the cleaner and method of cleaning may have to comply with certain health and environmental requirements. The object to be cleaned may only tolerate exposure to a cleaner of a certain pH or for a certain time without being harmed. The soil may e.g. require a cleaner with certain tensides or solvents to be removed from the object to be cleaned or at least to be made less visible or invisible.

[0003] In case of vehicles, particularly rail vehicles, soils arise e.g. from exposure to flash rust, dust generated by abrasion of brakes, rails, wheels, current collectors and overhead lines, inorganic dust containing aluminum, calcium or magnesium, and organic substances such as pollen, insects, oil and grease. The type and way of formation of the contamination on the surface where dirt is deposited under significant impact force, in combination with a high frequency of use of the vehicle as well as the exposure to any weather and temperature conditions can lead to a special contamination on a vehicle's surface difficult to remove and requiring specific cleaners and methods of cleaning. The large surface area of rail vehicles furthermore requires efficient and fast cleaning without extensive amounts of cleaners. The large amounts of waste water generated during cleaning of a vehicle's surface should not have adverse environmental effects.

[0004] Methods for cleaning of contaminated surfaces of trains have included the use of acid, alkaline or neutral cleaning compositions. With regard to acid cleaning compositions, DE 19651319 e.g. points out the use of phosphoric acid containing cleaning compositions. DD 47897, which is also directed to the cleaning of surfaces of trains, describes that acid cleaning compositions containing oxalic acid and phosphoric acid had been used. US 3,793,221 discloses a thickened acid cleaner concentrate composition for cleaning rail vehicles, the cleaner concentrate composition comprising an aqueous hydrochloric acid, a small amount (1 to 6 wt.-%) of an organic acid, e.g. oxalic acid, surfactants and water.

[0005] One difficulty with cleaning concentrates to be used for the cleaning of surfaces of vehicles is, however, their instability with respect to formation of precipitates which cause inhomogeneity and lead to clogged nozzles during e.g. pumping or spraying. In this respect, US 3,993,575 describes that normally up to 10 wt.-% of dicarboxylic acid had been the maximum amount in liquid cleaning composition concentrates based on solubility characteristics. US 3,993,575 thus proposed a cleaner for the cleaning of trains which comprises an aqueous solution of 5 to 30 % of a dicarboxylic acid, e.g. oxalic acid, and 3 to 15 % of an amine. The amine should partially neutralize the dicarboxylic acid. Stable cleaner concentrates should thus be obtained. The cleaner of US 3,993,575 also avoids mineral acids. The water content of the cleaner of US 3,993,575 is high, i.e. 44.5 to 90 %, and a dwell time of at least 3 minutes of the concentrate or a diluted composition is needed on the surface of the vehicle to be cleaned. This involves the risk that the cleaner may dry on the surface of the vehicle to be cleaned.

[0006] US 2003/0109402 and PCT/US2012/026668 describe highly concentrated oxalic acid compositions for lowering the alkalinity of a textile and cleaning of the inside of tubes of controlled atmosphere brazed aluminum heat exchangers of automobiles. The compositions contain a quaternary phosphonium compound (US 2003/0109402) or an azole compound (PCT/US2012/026668). Cleaning large surfaces of vehicles, particularly of rail vehicles, is not the focus of those documents.

[0007] In the field of surface cleaning of vehicles with its specific requirements due to the large surface, the special kind of soil and high cleaning effectiveness there is a need for a method of cleaning using a stable economical cleaning concentrate, Such concentrate and dilutions thereof should be easy and fast to prepare. Due to the concentrated nature of the cleaning concentrate transport and storage costs compared to voluminous diluted cleaning compositions should be reducible. The use of the cleaner concentrate for cleaning a surface of a vehicle should be efficient, time-wise and economically and the cleaning concentrate should be environmentally friendly. The cleaning compositions that can be prepared with such concentrates should provide excellent cleaning efficiency, in particular for vehicles with large surfaces, such as trains.

[0008] For the solution of this problem the invention suggests the process as defined in the claims.

[0009] The invention thus concerns a process for cleaning a surface of a vehicle, comprising providing a cleaning concentrate, diluting the cleaning concentrate to obtain a cleaning composition and applying the cleaning composition to the surface of the vehicle wherein the cleaning concentrate contains at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerine and at least 11 wt.-% of oxalic acid, wherein wt.-% is based on the total weight of the cleaning concentrate.

[0010] In this specification, "parts" and "%" are on a weight by weight basis, if nothing else is explicitly stated or evident for a skilled person in the specific context.

[0011] When it is referred to the cleaning of a surface of a vehicle this usually means cleaning of the outer surface of

the vehicle. This surface is normally exposed to weather during use of the vehicle and it is this surface which is easily soiled e.g. by flash rust, street dust, etc.

[0012] The cleaning concentrate may be applied as such on the surface of the vehicle and be diluted on the surface. This is considered as one possibility to apply the cleaning composition to the surface of the vehicle. Preferably, the cleaning concentrate is, however, first diluted to obtain a cleaning composition of a lower oxalic acid concentration compared with the cleaning concentrate and this cleaning composition is then applied to the surface of the vehicle for cleaning. The process according to the present invention thus includes a process as described herein before wherein the cleaning composition is applied to the surface of the vehicle either by applying the cleaning concentrate to the surface of the vehicle and diluting the cleaning concentrate on the surface of the vehicle to obtain a cleaning composition or by first diluting the cleaning concentrate to obtain a cleaning composition and then applying the cleaning composition to the surface of the vehicle. In a preferred process the cleaning concentrate is first diluted to obtain a cleaning composition before the cleaning composition is applied to the surface of the vehicle.

[0013] Dilution can be made e.g. with at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin. The cleaning composition obtained by dilution may e.g. have a concentration of 1.5 wt.-% to 3 wt.-% oxalic acid based on the total weight of the cleaning composition. It is also possible that the cleaning composition obtained by dilution has a concentration of only 0.3 wt.-% to 1.5 wt.-% oxalic acid based on the total weight of the cleaning composition. Preferably, dilution is made with water so that a cleaning composition with at least 50 wt.-% water, preferably at least 70 wt.-%, more preferably at least 85 wt.-% or even at least 90 wt.-%, based on the total weight of the cleaning composition is obtained.

[0014] In a preferred embodiment of the present invention, the cleaning concentrate contains at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin, at least 11 wt.-% oxalic acid, and at most 39 wt.-% water, wherein wt.-% is based on the total weight of the cleaning concentrate. Preferably, the water content in the cleaning concentrate used in the present invention is between 5-35 wt.-%. It can, for example, be between 10-25 wt.-% based on the total weight of the cleaning concentrate. Preferably only one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin is present in the cleaning concentrate used in the present invention. If only one of the members of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin is contained in the cleaning concentrate used in the present invention its concentration is preferably at least 40 wt.-% based on the total weight of the cleaning concentrate. Its concentration can also be 50 wt.-% based on the total weight of the cleaning concentrate or more. If two or more of the members of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin are present in the cleaning concentrate their concentration is preferably at least 40 wt.-% in total, preferably at least 50 wt.-% based on the total weight of the cleaning concentrate.

[0015] The cleaning concentrate used in the present invention can e.g. be prepared by dissolving oxalic acid in the at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin at a temperature of e.g. 30°C.The other components of the cleaning concentrate may then be added thereto. Preferably, the cleaning concentrate which is used in the present invention is prepared by dissolving oxalic acid dihydrate in the at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin at a temperature of e.g. 30°C and adding the remaining components of the cleaning concentrate thereto. The oxalic acid content of the cleaning concentrate used in the present invention is calculated on an anhydrous basis. Nevertheless, usually oxalic acid dihydrate is used to prepare the cleaning concentrate used in the present invention. If water is present in the cleaning concentrate it is preferred that at least 30 wt.-% of the water in the cleaning concentrate derives from oxalic acid dihydrate used to prepare the cleaning concentrate.

[0016] Preferably, the present invention concerns a process as described herein before wherein the cleaning concentrate contains at least 50 wt.-% of ethylene glycol, at least 15 wt.-% of oxalic acid and at most 30 wt.-% of water wherein wt.-% is based on the total weight of the cleaning concentrate.

[0017] The oxalic acid content in the cleaning concentrate used in the present invention can e.g. be between 11 wt.-% and 45 wt.-%. Preferably, the cleaning concentrate used in the present invention contains 15 wt.-% and 35 wt.-% oxalic acid based on the total weight of the cleaning concentrate. The cleaning concentrate may also contain between 15 wt.-% and 25 wt.-% or between 36 wt.-% and 45 wt.-% oxalic acid. Due to the highly concentrated cleaning concentrates used in the present invention only small amounts of the cleaning concentrate are necessary for cleaning a surface of a vehicle. In case of vehicles, particularly rail vehicles, which have large surface areas to be cleaned, this is advantageous. The amount of cleaning concentrate that has to be transported to the place of cleaning can be reduced. Dilution of the cleaning concentrate, preferably with water, to obtain large volumes of cleaning composition can be made directly at the place of cleaning.

[0018] The cleaning concentrate is in liquid form. It may be sprayed onto the prewetted vehicle's surface to be cleaned, whereby it is diluted or it may be sprayed on the dry surface of the vehicle to which also diluent may be applied. It may be brushed or rubbed in mechanically (to loosen strongly adhering dirt) and may be rinsed off thereafter. Rinsing and prewetting (if applicable) is preferentially done with water. Brushing, rubbing and rinsing may of course also be performed

in case the cleaning concentrate may be diluted first to obtain a liquid cleaning composition before the cleaning composition is applied to the surface of the vehicle.

[0019] Despite the high oxalic acid content, the cleaning concentrate used in the present invention is usually a solution free of precipitate at a temperature of 20°C. Usually, the oxalic acid in the cleaning concentrate used in the present invention is dissolved. The cleaning concentrate is preferably a solution that stays free of precipitate even after 14 days of storage of the solution at 20°C. Clogging of nozzles by precipitate during pumping or spraying of the cleaning concentrate can thus be avoided when using such cleaning concentrate. A homogenous solution free of precipitate also allows better dosing of the cleaning concentrate when it is diluted to obtain a cleaning composition. No time and energy-consuming warming of the cleaning concentrate before use in order to obtain a homogenous preparation usable for cleaning a vehicle's surface is necessary in the present invention as known for conventional cleaners.

[0020] More preferably, the cleaning concentrate which is used in the present invention is a solution stable against precipitation during storage for at least 14 days at 10°C or below. Even more preferably it is a solution stable against precipitation during storage for at least 14 days at 5°C or below. The cleaning concentrate which is used in the present invention may also be a solution stable against precipitation during storage for at least 14 days at 0°C or below or even at -10°C or below or -15°C or below.

[0021] Stable cleaning concentrates which can be used in the present invention can simply be made from oxalic acid or oxalic acid dihydrate and at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin. Preferably ethylene glycol is used as solvent for the oxalic acid or oxalic acid dihydrate to prepare the cleaning concentrate used in the present invention.

[0022] No further components are necessary to confer storage stability to the cleaning concentrate. While US 2003/0109402 purported the use of a quaternary phosphonium compound to reduce precipitation in an oxalic acid containing preparation, the cleaning concentrate used in the present invention preferably contains at most 1 wt.-% of a quaternary phosphonium compound, more preferably at most 0.0005 wt.-% of a quaternary phosphonium compound based on the total weight of the cleaning concentrate. Preferably, the cleaning concentrate used in the present invention contains no quaternary phosphonium compound.

[0023] The cleaning concentrate used in the present invention does not need to contain an amine, either. US 3,993,575 describes that the addition of an amine to an oxalic acid containing preparation may raise the pH and thus increase solubility of oxalic acid. The inventors of the present invention have, however, found that storage-stable cleaning concentrates containing high amounts of oxalic acid can be achieved without using an amine for use in the process of the present invention.

[0024] The present invention thus also concerns a process as described herein before wherein the cleaning concentrate contains less than 3 wt.-% of an amine wherein wt.-% is based on the total weight of the cleaning concentrate. It is also possible that the cleaning concentrate used in the present invention contains less than 1.5 wt.-% of an amine. It may also contain less than 0.5 wt.-% of an amine or no amine at all.

[0025] It has been found that in the process according to the present invention the cleaning concentrate does not have to contain a corrosion inhibitor, such as e.g. benzotriazole. The invention thus also concerns a process as described herein before wherein the cleaning concentrate contains at most 0.1 wt.-%, preferably at most 0.0005 wt.-% of an azole compound based on the total weight of the cleaning concentrate. More preferably, the cleaning concentrate used in the present invention contains no azole compound. The avoidance of azole compounds is advantageous as those compounds may be of low or no biodegradability which is environmentally unfriendly.

[0026] In one embodiment, the present invention concerns a process as described herein before wherein the cleaning concentrate contains no quaternary phosphonium compound, no azole compound and less than 3 wt.-% of an amine wherein wt.-% is based on the total weight of the cleaning concentrate, preferably no amine.

[0027] Optionally, the cleaning concentrate used in the present invention contains a tenside. One or more tensides may be contained in the cleaning concentrate. The tenside may e.g. be 4-sec-alkyl-(C10-C13)-benzenesulfonic acid, fatty alcohol polyalkylene glycol ether or sodium N-(2-carboxyethyl)-N-dodecyl-beta-alaninate. These tensides are e.g. sold as Lutensit A-LBS, Propetal 105 and Amphotensid CCF, respectively.

[0028] It is also possible that the cleaning concentrate used in the present invention contains one or more additional acids. This can be a mineral acid(s). Preferably, the cleaning concentrate used in the present invention contains ortho phosphoric acid. The additional acid besides oxalic acid which can be contained in the cleaning concentrate is e.g. contained in a concentration of 5 wt.-% to 15 wt.-% based on the total weight of the cleaning concentrate. In one embodiment the cleaning concentrate used in the present invention contains ethylene glycol, at least 11 wt.-% oxalic acid and at most 39 wt.-% water, wherein wt.-% is based on the total weight of the cleaning concentrate, and 4-sec-alkyl-(C10-C13)-benzenesulfonic acid, ortho phosphoric acid and optional other known additives for cleaning compositions for cleaning the surface of trains, such as wetting agents and here reference is made to the commercial product Rewocare 755, obtainable form the company Evonik Industries AG, 45127 Essen, Germany.

[0029] The cleaning concentrate used in the present invention may be relatively acidic for achieving good cleaning results. A dilution of 1 volume of cleaning concentrate with 8 volumes of water may, for example, have a pH of 0.2 to 2.

When the pH is indicated in this specification it is measured at 25°C if it is not stated otherwise. The pH of a dilution of 1 volume of cleaning concentrate used in the present invention with 8 volumes of water may also e.g. have a pH of 0.2 to 1.4. Preferably, the present invention concerns a process as described herein before wherein a dilution of 1 volume of the cleaning concentrate with 8 volumes of water has a pH of 0.2 to 1.2. The dilution of 1 volume of cleaning concentrate with 8 volumes of water may e.g. have a pH of 0.6 to 1.2 or 0.7 to 1.0. In one embodiment the present invention is directed to a process as described herein before wherein the cleaning concentrate is diluted to result in a cleaning composition with at least 85 wt.-% water based on the total weight of the cleaning composition and a pH between 0.2 and 1.2, preferably between 0.6 and 1.2, and this cleaning composition is applied to the surface of the vehicle.

[0030] Due to the large amounts of cleaning concentrate needed for cleaning a vehicle's surface the use of an environmentally friendly cleaning concentrate is of particular concern. The present invention meets these concerns. Oxalic acid is biodegradable. The cleaning composition obtained by dilution of the cleaning concentrate may be collected together with rinsing water. Oxalic acid may be removed from this waste water by addition of hydrogen peroxide. The worked up waste water may be reused in the cleaning process, The present invention thus also concerns a process as described herein before for cleaning a surface of a vehicle comprising i) providing a cleaning concentrate as defined herein before and diluting the cleaning concentrate to obtain a cleaning composition wherein the cleaning concentrate is applied directly to the surface of the vehicle and diluted thereon or wherein the cleaning concentrate is diluted to obtain a cleaning composition before the cleaning composition is applied to the surface of the vehicle, ii) rinsing the surface with water, iii) collecting the cleaning composition together with the water used for rinsing and iv) removing oxalic acid therefrom by addition of hydrogen peroxide.

[0031] Due to the composition and stability of the cleaning concentrate against precipitation, the cleaning concentrate may be used for cleaning a vehicle's surface at low surrounding temperatures in a preferred embodiment of the present invention. While cleaning at low surrounding temperatures is not important for cleaning most substrates, it is advantageous for cleaning the surface of a vehicle. The present invention may allow the outdoor cleaning or indoor cleaning in unheated surroundings of e.g. a rail vehicle in the winter when usually only highly aggressive winter cleaners (containing e.g. hydrochloric acid, sulphuric acid and/or amido sulfonic acid) are used.

[0032] The invention thus preferably also concerns a process as described herein before for cleaning the surface of a vehicle at a surrounding temperature of 5°C or lower, e.g. at 0°C-5°C. The present invention also concerns a process as described herein before wherein the surface of the vehicle has a temperature of 5° or lower, e.g. 0°C-5°C. The cleaning concentrate used for cleaning the surface of a vehicle in the process of the present invention may have a temperature of 5°C or below, e.g. 0°C-5°C.

[0033] Another problem of conventional cleaners that is overcome by the present invention is the risk of drying of the cleaner on the substrates to be cleaned. While drying of the cleaner may be no problem when cleaning the inside of an element, where e.g. evaporation of a solvent of the cleaner is restricted, it may, however, be problematic when cleaning the surface of a vehicle which may heat up e.g. upon sun exposure in the summer significantly. The problem of drying of a cleaner on the surface of a vehicle aggravates when a long dwell time is needed on the surface for the cleaner to take effect. In a cleaning line for rail vehicles, a cooling stand may thus become necessary where the vehicle's surface is cooled with water. This requires extra-space in the cleaning line, large amounts of cooling water and additional equipment for pumping and spraying the cooling water.

[0034] Due to the composition of the cleaning concentrate used in the present invention it is no problem if the surface of the vehicle to be cleaned in the process of the present invention is hot. The present invention is thus also directed to a process as described herein before wherein the surface of the vehicle has a temperature of 30°C or higher, preferably of 40°C or higher. The surface of the vehicle can e.g. have a temperature of 30°C to 60°C. The cleaning composition obtained by diluting the cleaning concentrate preferably comprises at least 2 wt.-%, more preferably at least 4 wt.-% and even more preferably at least 6.57 wt.-% of one member or a mixture of members of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerin based on the total weight of the cleaning composition in the case of hot surfaces.

[0035] In a preferred embodiment the present invention concerns a process as described herein before wherein the surface of the vehicle has a temperature of 5°C or lower or of 30°C or higher, preferably of 40°C or higher.

[0036] The present invention allows for very efficient cleaning as only a short dwell time on the surface of the vehicle to be cleaned is needed for the cleaning composition obtained by diluting the cleaning concentrate to be effective. The present invention therefore also concerns a process as described herein before wherein the dwell time of the cleaning composition on the surface of the vehicle is 2 min or less. Preferably the dwell time is 1 min or less. When considering these dwell times, the cleaning concentrate should preferably be diluted to obtain the cleaning composition before the cleaning composition is applied to the surface of the vehicle. As dwell time the time is considered during which the cleaning composition is in contact with the surface being cleaned. It may be removed from the surface of the vehicle by rinsing the surface of the vehicle with water.

[0037] The present invention allows high throughput of rail vehicles through cleaning lines. The process according to the present invention e.g. allows a velocity of a train moving through a cleaning line of 15.2 m/min. Cleaning of a surface

of a vehicle is usually performed within an automated cleaning line in the present invention.

[0038] Conventional cleaning methods are also performed in automated cleaning lines, but the cleaning result is usually not acceptable, so that in addition to the automated process a manual basic cleaning is also performed. Such a manual basic cleaning is not required in the process of the present invention to achieve acceptable cleaning results.

[0039] Examples of vehicles the surface of which can be cleaned according to the process of the present invention include vehicles such as a rail vehicle (e.g. train or tram), a car, a motorcycle, a truck, and a bus. The surface itself may e.g. be a metal surface, preferably a coated surface e.g. with paint (lacquer), an anodized surface or a stainless steel surface. Preferably, the present invention concerns a process as described herein before wherein the vehicle is a rail vehicle, preferably a train.

[0040] One kind of soil that should be particularly removed from the surface of a vehicle by the process according to the present invention is rust (hydrated iron oxides). In one embodiment the present invention thus concerns a process as described herein before wherein the surface of the vehicle comprises rust and the cleaning process encompasses removing the rust from the surface of the vehicle.

[0041] It is possible to treat a vehicle's surface with further cleaning and/or additive compositions after having applied the cleaning concentrate to the surface and having diluted it on the surface or after having applied the cleaning composition obtained by diluting the cleaning concentrate to the surface of the vehicle. This can lead to further improved and/or longer-lasting cleanliness of the vehicle's surface. The present invention thus also concerns a process as described herein before comprising (i) applying a cleaning composition containing at least one polypeptide, wherein the total amount of polypeptide in the cleaning composition is from 9.9*10-6 wt.-% to 1.2*10-2 wt.-% based on the total weight of this cleaning composition, to the surface of the vehicle and/or (ii) applying a drying aid (or rinse aid) to the surface of the vehicle.

[0042] A polypeptide as used herein also encompasses proteins which are long chained polypeptides. Preferably, the at least one polypeptide as used herein has a molecular weight (MR) of at least 1000 g/mol and not more than 600000 g/mol, more preferably, the molecular weight is from 20000 g/mol to 300000 g/mol. Preferably, all polypeptides in the second cleaning composition have a molecular weight (M_R) of at least 1000 g/mol and not more than 600000 g/mol, more preferably from 20000 g/mol to 600000 g/mol, e.g. from 20000 g/mol to 300000 g/mol. The at least one polypeptide as used herein is preferably gelatine. The nitrogen content of the gelatine is preferably 16 wt.-% to 19 wt.-%. The hydroxyprolin content is preferably 10 wt.-% to 15 wt.-%. As the at least one polypeptide particularly gelatine with one or more of the following features has proved to be successful:

Gel strength (according to AOAC): ≥ 120 g Bloom
Viscosity (6.67 %; 60°C): 3.00 - 4.00 mPa*s
pH (6.67 %; 60°C): 5.50-6.00
transmission (620 nm 6.67 %): ≥ 88 %
transmission (450 nm 6.67 %): ≥ 68 %
conductivity (1.00%; 30°C): ≤ 150 μS/cm
Calcium (Ca complexometric): ≤ 750 ppm

[0043] Particularly good cleaning results were obtained with the gelatine having the described features.

[0044] Drying aids are commercially available from different companies. In the present invention the drying aids are preferably selected from a drying aid containing at least one tenside and/or at least one hydrophilic polymer. A tenside as used herein is considered a compound having amphiphilic properties. For the purpose of the invention a compound which might be considered as both, a tenside or a polymer is designated as tenside. The tenside is preferably a fatty alcohol polyalkylene glycol ether. For example, a C8-C18 alcohol polyalkylene glycol ether is used as drying aid in the present invention. The fatty alcohol polyalkylene glycol ether has preferably less than 100 C-atoms. The hydrophilic polymer is preferably selected from the group consisting of polyvinylalcohol, polyvinylacetate, poly(meth)acrylate, poly(meth)acrylic acid, polyurethane, polyisocanate, polyisothiocyanate and polysuccinimidester. It is more preferably selected from the group consisting of polyvinylalcohol, polyvinylacetate, poly(meth)acrylate and poly(meth)acrylic acid. Preferably, the total amount of tenside contained in the drying aid is from 10^{-8} wt.-% to 10^{-6} wt.-%, more preferably from $5*10^{-8}$ wt.-% to $5*10^{-7}$ wt.-% based on the total weight of the drying aid. Preferably, the total amount of hydrophilic polymer contained in the drying aid is from 10^{-8} wt.-% to 10^{-6} wt.-%, more preferably from $5*10^{-8}$ wt.-% to $5*10^{-7}$ wt.-% based on the total weight of the drying aid. If both, a tenside and a polymer are contained in the drying aid, the total amount of both in the drying aid is from 10^{-8} wt.-% to 10^{-6} wt.-% each, more preferably from $5*10^{-8}$ wt.-% to $5*10^{-7}$ wt.-% each based on the total weight of the drying aid. Most preferably, the drying aid contains a tenside and no polymer.

[0045] A preferred drying aid of the present invention can be obtained by diluting the commercial product Bedos 690 (Boss Chemie, Wittenbach, Switzerland).. For use in the process of the present invention Bedos 690 is diluted with water prior to its application. The drying aid is usually diluted as known in the art. For example, the product Bedos 690 is diluted with about 10000000 parts of water (per part of Bedos 690) for application.

[0046] The different treatments of the vehicle's surface should be performed in the described order. Additional inter-

mediate steps are of course possible, e.g. rinsing with fresh water or process water.

[0047] Use of the cleaning concentrate in a process as described herein before is also part of the present invention.

[0048] The following examples are intended to illustrate the invention without however limiting it.

[0049] Figure 1 shows schematically a conventional cleaning line that has been used for cleaning a train in the following examples.

Example 1

Cleaning concentrate

[0050] A cleaning concentrate was prepared as follows: 27 parts by weight of oxalic acid dihydrate were dissolved in 59.21 parts by weight of ethylene glycol at about 30°C. 13.5 parts by weight of ortho phosphoric acid 75%, 0.27 parts by weight of alkyl benzene sulfonic acid and 0.02 parts by weight of Rewocare 755 (Evonic Industries, Germany) were added thereto. A clear solution was obtained.

[0051] Samples of the cleaning concentrate were stored at temperatures of -5°C, -10°C and -15°C for 14 days each. After storage the samples showed no change such as turbidity, precipitation etc. The samples were still clear solutions. Another sample of the cleaning concentrate was stored at 60°C for 24 h and subsequently slowly cooled to 5°C. No layering, precipitation and color change could be observed in the sample.

Cleaning composition

[0052] For cleaning a train as described below, 1 part by volume of the cleaning concentrate was mixed with 8 parts by volume of water (when it is referred to water without further specifying the type of water, fresh water is meant hereafter) to obtain a cleaning composition that was applied to a train's surface. The cleaning composition had a pH of 0.9 (at 25°C).

Drying aid

[0053] A drying aid concentrate was prepared as follows: 0.454 parts by weight of Bedos 690 (Boss Chemie, Wittenbach, Switzerland) were mixed with 99.496 parts by weight of water. 0.05 parts by weight of a preservative (Parmetol A 26, Schülke & Mayr GmbH, Norderstedt, Germany) were added to avoid formation of streaks in the composition and development of bad odor.

[0054] For cleaning a train as described below, 1 part by volume of the drying aid concentrate was mixed with 46500 parts by volume of water to obtain the drying aid as applied on the train surface in the cleaning process. Alternatively, the drying aid could be prepared directly in the concentration of use on the train surface, thus omitting the preparation of the drying aid concentrate and its dilution.

Cleaning process

[0055] A conventional cleaning line (Figure 1) for trains was used to show the effectiveness of the process for cleaning a train. The cleaning concentrate was diluted to result in the cleaning composition as described above and the cleaning composition was applied to the surface of the train.

[0056] A standard train (two-part diesel railcar (series 628 by Düwag, Waggon-Union, AEG i.a.)) having a length of 46 m was used for this example. The train had visible contamination on the train surface. The train moved through the cleaning line with a constant velocity of 15.2 m/min (by a tow carriage via a rope). The cleaning line had a length of 70 m and the complete cleaning cycle was finished after 23.63 minutes.

[0057] At the precleaning stand, the cleaning composition (composed of 1 part by volume of the cleaning concentrate and 8 parts by volume of water) was sprayed onto the train. After 3.3 m the front of the train reached washing stand A where the side area of the train was brushed via side brushes (without the use of any additional water).

[0058] In between, after the front of the train had passed washing stand A by about 3-4 m, the entire process (spray arch at precleaning stand and brushing via side brushes at washing stand A) was interrupted and the front of the train was brushed via the top brush of cleaning stand A

[0059] (without the use of any additional water) by relative movement of washing stand A to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes. Due to the ethylene glycol content in the cleaning composition, a lubricating film was created on the surface so that no damage occurs to the surface when brushing (without additional water). The cleaning composition did not dry on the surface.

[0060] Subsequently, the train was moved further through the cleaning line and reached washing stand B after 46 m. At washing stand B the train was brushed with the side brushes. Immediately after washing stand B the surface of the train was rinsed with process water at postcleaning stand I.

[0061] After 6 m the train reached postcleaning stand II, where it was rinsed with drying aid (composed of 1 part by volume of the drying aid concentrate and 46500 parts by volume of water). After 3 more meters the train was again rinsed with process water at postcleaning stand III.

[0062] After the train had passed washing stand B, the entire process was interrupted. The rear of the train was brushed via the top brush by relative movement of washing stand B to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes.

[0063] Thereafter, the train was further moved through the cleaning line so that the rear of the train finally also passed the postcleaning stands and the entire train left the cleaning line after 23.63 min.

[0064] Postcleaning stand I is 62.9 meter after the precleaning stand. Most of the surface of the train was thus in contact with cleaning components for 4.14 min before they were rinsed off (dwell time).

[0065] From the following Table I the details regarding the amount of composition sprayed, spray pressure, spray temperature and spray time etc. can be seen.

Table I (averaged values obtained from a series of measurements (10))

Length of train 46 m Length of cleaning line 70 m Ambient temperature Velocity of train moving through cleaning line 15.2 m/min	Duration/min	Pressure	Water (fresh water)/l	Process water/l	Cleaning concentrate/l	Drying aid concentrate/l
Precleaning stand	3.03	3.75 bar	87.12		10.88	
Washing stand A / front of train	6.5/8*	3.75 bar	0			
Washing stand A / sides of train	3.03	3.75 bar	0			
Washing stand B / rear of train	6.5/8*	3.75 bar	165			
Washing stand B / sides of train	3.03	3.75 bar	80			
Postcleaning stand I	3.03	3.75 bar		557		
Postcleaning stand II	3.03	3.75 bar	312			0.0067
Postcleaning stand III	3.03	3.75 bar		599		
Passing entire length of cleaning line	4.6					
In total	**23.63**		**644.12**	**1156**	**10.88**	**0.0067**

*brushes moved for 6.5 min out of 8 min

[0066] After the train had left the cleaning line it had a clean and shiny surface and showed no visible contaminations.

Example 2

[0067] A first cleaning concentrate and first cleaning composition as well as a drying aid concentrate and drying aid were prepared as described above in example 1.

Second cleaning concentrate

[0068] A second cleaning concentrate was prepared as follows: 10 parts by weight of potassium hydrogen tartrate were mixed with 35 parts by weight of water at about 40°C. The forming precipitate was dissolved by addition of sodium hydroxide until a pH of 10.2 was obtained. 1.5 parts by weight of alkyl ether sulfate C12-14 with EO, sodium salt (content ≥ 20 % - < 30 %) (Texapon NSO UP), 2.1 parts by weight of isotridecanol, ethoxylated (>5-20 EO) (Marlipal O 13/90), 7 parts by weight of sodium cumene sulfonate (content ≥ 25 % - < 50 %) (Lutensit TC-CS 40), 0.07 parts by weight of Rewocare 755 (Evonik Industries, Germany), 0.02 parts by weight of orange terpenes, 3 parts by weight of ethylene glycol and 2 parts by weight of butyl diglycol were added to the mixture. Furthermore, 0.038 parts by weight of gelatine were added to the mixture. Therefore gelatine (Novotec, ® 100, Gelita Deutschland GmbH, Eberbach, Germany) was soaked in cold water for 20 min and subsequently dissolved at 60°C and this preparation was added to the mixture. Finally, 0.05 parts by weight of Parmetol A 26 (Schülke & Mayr GmbH, Norderstedt, Germany) were added to the mixture and the pH of the mixture was adjusted to < 9.5. In total (including the sodium hydroxide used in the beginning of the preparation of the second cleaning concentrate, see above), 2.2 - 2.5 parts by weight of sodium hydroxide were thus

used to prepare the second cleaning concentrate. The remaining parts by weight of the cleaning concentrate is water. A dye may be added.

Second cleaning composition

[0069] For cleaning a train as described below, 1 part by volume of the second cleaning concentrate was diluted with 50 part by volume of water to obtain the second cleaning composition as applied on the train surface in the cleaning process. Alternatively, the second cleaning composition could be prepared directly in the concentration of use on the train surface, thus omitting the preparation of the second cleaning concentrate and its dilution.

Cleaning process

[0070] A conventional cleaning line (Figure 1) for trains was used again in this example and the same standard train as used in example 1, which showed visible contamination on the train surface, was used. The train moved through the cleaning line with a constant velocity of 15.2 m/min (by a tow carriage via a rope). The cleaning line had a length of 70 m and the complete cleaning cycle was finished after 23.63 minutes.

[0071] In this experiment, first cleaning composition (composed of 1 part by volume of the cleaning concentrate and 16 parts by volume of water) was sprayed onto the train at the precleaning stand. After 3.3 m the front of the train reached washing stand A where the first cleaning composition (composed of 1 part by volume of the first cleaning concentrate and 16 parts by volume of water) was applied to the entire side area of the train brushed in via side brushes.

[0072] In between, after the front of the train had passed washing stand A by about 3-4 m, the entire process (spray arch at precleaning stand and application of the cleaning composition and brushing in via side brushes at washing stand A) was interrupted and the second cleaning composition (composed of 1 part by volume of the second cleaning concentrate and 50 parts by volume of water) was applied to the front of the train and brushed in via the top brush of cleaning stand A by relative movement of washing stand A to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes.

[0073] Subsequently, the train was moved further through the cleaning line and reached washing stand B after 46 m. At washing stand B the train was brushed with the side brushes. Immediately after washing stand B the surface of the train was rinsed with process water at postcleaning stand I.

[0074] After 6 m the train reached postcleaning stand II, where it was rinsed with drying aid (composed of 1 part by volume of the drying aid concentrate and 46500 parts by volume of water). After 3 more meters the train was again rinsed with process water at postcleaning stand III.

[0075] After the train had passed washing stand B, the entire process was interrupted. _The rear of the train was brushed via the top brush by relative movement of washing stand B to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes.

[0076] Thereafter, the train was further moved through the cleaning line so that the rear of the train finally also passed the postcleaning stands and the entire train left the cleaning line after 23.63 min

[0077] From the following Table II the details regarding the amount of composition sprayed, spray pressure, spray temperature and spray time etc. can be seen.

Table II (averaged values obtained from a series of measurements (10))

Length of train 46 m Length of cleaning line 70 m Ambient temperature Velocity of train moving through cleaning line 15.2 m/min	Duration/min	Pressure	Water (fresh water)/l	Process water/l	1. Cleaning concentrate/l	2. Cleaning concentrate/l	Drying aid concentrate/l
Precleaning stand	3.03	3.75 bar	87.12		5.45		
Washing stand A / front of train	6.5/8*	3.75 bar	110			2.2	
Washing stand A / sides of train	3.03	3.75 bar	28,24		1.76		
Washing stand B / rear of train	6.5/8*	3.75 bar	165				
Washing stand B / sides of train	3.03	3.75 bar	80				
Postcleaning stand I	3.03	3.75 bar		557			
Postcleaning stand II	3.03	3.75 bar	312				0.0067
Postcleaning stand III	3.03	3.75 bar		599			
Passing entire length of cleaning line	4.6						
In total	**23.63**		**784.12**	**1156**	**7.21**	**2.2**	**0.0067**

*brushes moved for 6.5 min out of 8 min

[0078] After the train had left the cleaning line it had a clean and shiny surface and showed no visible contaminations.

Example 3

[0079] A first cleaning concentrate and first cleaning composition as well as a drying aid concentrate and drying aid were prepared as described above in example 1.

[0080] A second cleaning concentrate was prepared as describe above in example 2.

Second cleaning compositions

[0081] For cleaning a train as described below, the second cleaning concentrate was diluted with water as follows to obtain the second cleaning compositions (table III) as applied at the different stands on the train surface in the cleaning process, see below:

Table III (averaged values obtained from a series of measurements (10))

	Second cleaning concentrate (parts by volume)	Water (parts by volume)
Washing stand A – top brush	1	50
Washing stand B – top brush	1	85
Washing stand B – side brushes	1	85

[0082] Alternatively, second cleaning compositions could be prepared directly in the concentrations of use on the train surface, thus omitting the preparation of a second cleaning concentrate and its dilution.

Cleaning process

[0083] A conventional cleaning line (Figure 1) for trains was used again in this example and the same standard train as used in example 1, which showed visible contamination on the train surface, was used. The train moved through the cleaning line with a constant velocity of 15.2 m/min (by a tow carriage via a rope). The cleaning line had a length of 70

m and the complete cleaning cycle was finished after 23.63 minutes.

[0084] In this experiment, first cleaning composition (composed of 1 part by volume of the first cleaning concentrate and 8 parts by volume of water) was sprayed onto the train (side, front, rear) at the precleaning stand. After 3.3 m the front of the train reached washing stand A where first cleaning composition (composed of 1 part by volume of the first cleaning concentrate and 8 parts by volume of water) was applied to the entire side area of the train and brushed in via side brushes.

[0085] In between, after the front of the train had passed washing stand A by about 3-4 m, the entire process (spray arch at precleaning stand and application of first cleaning composition and brushing in via side brushes at washing stand A) was interrupted and second cleaning composition (composed of 1 part by volume of the second cleaning concentrate and 50 parts by volume of water) was applied to the front of the train and brushed in via the top brush of cleaning stand A by relative movement of washing stand A to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes, which could, however, also be shortened if desired while still obtaining good cleaning results.

[0086] Subsequently, the train was moved further through the cleaning line and reached washing stand B after 46 m. At washing stand B, second cleaning composition (composed of 1 part by volume of the second cleaning concentrate and 85 parts by volume of water) was applied to the train and brushed in via the side brushes. Immediately after washing stand B the surface of the train was rinsed with process water at postcleaning stand I.

[0087] After 6 m the train reached postcleaning stand II, where it was rinsed with drying aid (composed of 1 part by volume of the drying aid concentrate and 46500 parts by volume of water). After 3 more meters the train was again rinsed with process water at postcleaning stand III.

[0088] After the train had passed washing stand B, the entire process was interrupted and second cleaning composition (composed of 1 part by volume of the second cleaning concentrate and 85 parts by volume of water) was applied to the rear of the train and brushed in via the top brush by relative movement of washing stand B to the train which was stopped in the cleaning line for this procedure (the tow carriage stands still). This procedure took 8 minutes, which could, however, also be shortened if desired while still obtaining good cleaning results. Thereafter, the train was further moved through the cleaning line so that the rear of the train finally also passed the postcleaning stands and the entire train left the cleaning line after 23.63 min.

[0089] From the following Table IV the details regarding the amount of composition sprayed, spray pressure, spray temperature and spray time etc. can be seen.

Table IV (averaged values obtained from a series of measurements (10))

Length of train 46 m Length of cleaning line 70 m Ambient temperature Velocity of train moving through cleaning line 15.2 m/min	Duration/min	Pressure	Water (fresh water)/l	Process water/l	1. Cleaning concentrate/l	2. Cleaning concentrate/l	Drying aid concentrate/l
Precleaning stand	3.03	3.75 bar	87.12		10.88		
Washing stand A / front of train	6.5/8*	3.75 bar	110			2.2	
Washing stand A / sides of train	3.03	3.75 bar	26.67		3.33		
Washing stand B / rear of train	6.5/8*	3.75 bar	163			1.92	
Washing stand B / sides of train	3.03	3.75 bar	78.7			0.92	
Postcleaning stand I	3.03	3.75 bar		557			
Postcleaning stand II	3.03	3.75 bar	312				0.0067
Postcleaning stand III	3.03	3.75 bar		599			
Passing entire length of cleaning line	4.6						
In total	**23.63**		**777.49**	**1156**	**14.21**	**5.04**	**0.0067**

*brushes moved for 6.5 min out of 8 min

[0090] After the train had left the cleaning line it had a clean and shiny surface and showed no visible contaminations.

[0091] The train could then be used in a conventional manner for 28 days before cleaning of the train was necessary again.

Claims

1. Process for cleaning a surface of a vehicle, comprising providing a cleaning concentrate, diluting the cleaning concentrate to obtain a cleaning composition and applying the cleaning composition to the surface of the vehicle, wherein the cleaning concentrate contains at least one member of the group consisting of ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol and glycerine and at least 11 wt.-% of oxalic acid, wherein wt.-% is based on the total weight of the cleaning concentrate.

2. Process according to claim 1 wherein the cleaning composition is applied to the surface of the vehicle either by applying the cleaning concentrate to the surface of the vehicle and diluting the cleaning concentrate on the surface of the vehicle to obtain a cleaning composition or by first diluting the cleaning concentrate to obtain a cleaning composition and then applying the cleaning composition to the surface of the vehicle.

3. Process according to claim 1 or 2 wherein the cleaning concentrate contains at most 39 wt.-% of water, wherein wt.-% is based on the total weight of the cleaning concentrate.

4. Process according to any of claims 1-3 wherein the cleaning concentrate contains at least 50 wt.-% of ethylene glycol, at least 15 wt.-% of oxalic acid and at most 30 wt.-% of water wherein wt.-% is based on the total weight of the cleaning concentrate.

5. Process according to any of claims 1-4 wherein the cleaning concentrate contains 15 wt.-% to 35 wt.-% oxalic acid wherein wt.-% is based on the total weight of the cleaning concentrate.

6. Process according to any of claims 1-5 wherein the cleaning concentrate contains no quaternary phosphonium compound.

7. Process according to any of claims 1-6 wherein the cleaning concentrate contains less than 3 wt.-% of an amine wherein wt.-% is based on the total weight of the cleaning concentrate.

8. Process according to any of claims 1-7 wherein the cleaning concentrate contains no azole compound.

9. Process according to any of claims 1-8 wherein the cleaning concentrate contains a tenside.

10. Process according to any of claims 1-9 wherein the cleaning concentrate contains ortho phosphoric acid.

11. Process according to any of claims 1-10 wherein a dilution of 1 volume of cleaning concentrate with 8 volumes of water has a pH of 0.2 to 1,2.

12. Process according to any of claims 1-11 wherein the surface of the vehicle has a temperature of 5°C or lower or of 30°C or higher, preferably of 40°C or higher.

13. Process according to any of claims 1-12 wherein the dwell time of the cleaning composition on the surface of the vehicle is 2 min or less.

14. Process according to any of claims 1-13 wherein the vehicle is a rail vehicle, preferably a train.

15. Process according to any of claims 1-14 wherein the surface of the vehicle comprises rust and the cleaning process encompasses removing the rust from the surface of the vehicle.

16. Process according to any of claims 1-15 comprising (i) applying a cleaning composition containing at least one polypeptide, wherein the total amount of polypeptide in the cleaning composition is from $9.9*10^{-6}$ wt.-% to $1.2*10^{-2}$ wt.-% based on the total weight of this cleaning composition, to the surface of the vehicle and/or (ii) applying a drying aid to the surface of the vehicle.

17. Use of a cleaning concentrate in a process as defined in any of claims 1-16.

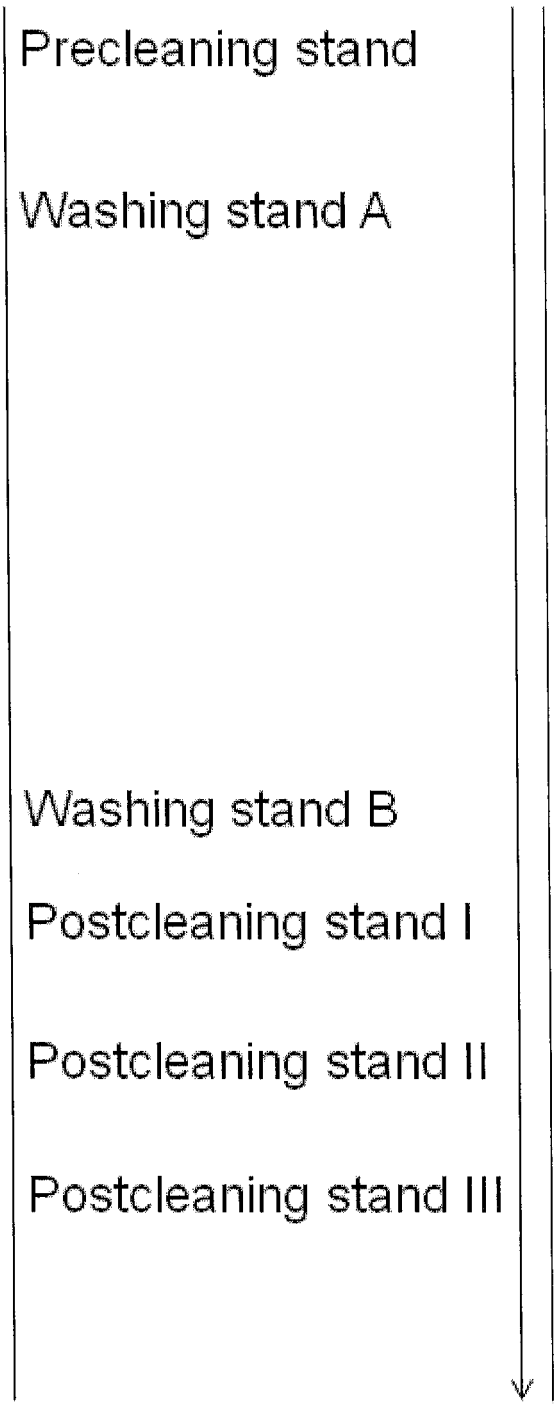
Precleaning stand
Washing stand A
Washing stand B
Postcleaning stand I
Postcleaning stand II
Postcleaning stand III

Figure 1

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EUROPEAN SEARCH REPORT

Application Number
EP 13 17 4563

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C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	30 September 2013	Péntek, Eric

CATEGORY OF CITED DOCUMENTS

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