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(54) IMPROVED PREVENTION OF WATER MARKS AND SPLASH MARKS

(57) The need for an acidic hard surface cleaning compositions which provides further improvements in the prevention of water marks and splash marks, is met by formulating the hard surface cleaning combination using polyquaternium-95.

EP 3 569 681 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to the use of polyquaternium-95 in acidic liquid compositions to prevent or reduce water-marks and splash marks on the treated surface.

BACKGROUND OF THE INVENTION

[0002] Limescale deposits are formed due to the fact that tap water contains a certain amount of solubilised ions, which upon water evaporation eventually deposit as salts, such as calcium carbonate on hard surfaces. These visible limescale deposits result in hard deposits around taps, sink holes, and the like, but also splash marks where water has sprayed and then dried. The limescale formation and deposition phenomenon is even more acute in places where water is particularly hard. Acidic liquid compositions for cleaning limescale from hard-surfaces have been disclosed in the art.
Such acidic cleaning compositions react with the limescale in order to remove such unsightly deposits. Surface modification polymers, such as polyvinyl pyrrolidone and copolymers thereof, have also been added to acidic cleaners, to prevent limescale from tightly bonding to the treated surface as hard water dries on the treated surface, for instance, after taking a shower. However, while surface modification polymers prevent limescale from binding strongly to the treated surface, they also typically make the surface more hydrophobic, resulting in beading of water on the treated surface. As the water-beads dry, the limescale precipitates onto the surface leaving unsightly water-marks and splash marks.

[0003] Hence, a need remains for improved limescale prevention onto the treated surface, while also minimizing water-marks and splash-marks.

[0004] US9226641 and US8563496 relates to acidic hard surface cleaning compositions comprising a malodor control component, in which the composition can optionally comprise surface modifying polymers such as copolymers of vinylpyrrolidone and zwitterionic surface modifying polysulphobetaine copolymers. WO200292747 relates to a method of washing cookware/tableware in an automatic dishwashing machine, wherein the dishwashing composition can optionally comprise zwitterionic surfactants such as the betaines and sultaines. US2014080748, US20050046064, and US20150202142 disclose alkaline compositions which can comprise sulphobetaine surfactant and polymeric crystal growth inhibitors.

SUMMARY OF THE INVENTION

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[0005] The present invention relates to the use of polyquaternium-95 in a hard surface cleaning composition to prevent or reduce water-marks or splash marks on the treated surface.

DETAILED DESCRIPTION OF THE INVENTION

[0006] The incorporation of polyquaternium-95 into hard surface cleaning compositions has been found to prevent and reduce water-marks and splash marks on hard surfaces treated by the cleaning composition. It is believed that polyquaternium-95 results in limescale precipitating as finer droplets which disperse light less and hence results in less visible water-marks and splash marks.

[0007] As defined herein, "essentially free of a component means that no amount of that component is deliberately incorporated into the composition. Preferably, "essentially free of a component means that no amount of that component is present in the composition.

[0008] As defined herein, "stable" means that no visible phase separation is observed for a premix kept at 25°C for a period of at least two weeks, or at least four weeks, or greater than a month or greater than four months, as measured using the Floc Formation Test, described in USPA 2008/0263780 A1.

[0009] All percentages, ratios and proportions used herein are by weight percent of the composition, unless otherwise specified. All average values are calculated "by weight" of the composition, unless otherwise expressly indicated.

[0010] All ratios are calculated as a weight/weight level of the active material, unless otherwise specified.

[0011] All measurements are performed at 25°C unless otherwise specified.

[0012] Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

[0013] By "molar mass" it is meant herein unless otherwise stated, the average molar mass in absolute mass, expressed in g/mol. For polymers, this can be determined by gel permeation chromatography (GPC), preferably using GPC-LS (light scattering), such as the G1260 Infinity II Multi-Detector GPC/SEC System from Agilent Technologies. For water-

soluble polymers, water can be used as a solvent (with the addition of methanol as needed up to 50% by weight), using an Agilent PL aquagel-OH column. For non-aqueous polymers, toluene can be used as a solvent, using an Agilent PLgel column.

5 The hard surface cleaning composition

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[0014] The compositions of use in the present invention are designed as hard surfaces cleaners. The compositions are typically liquid compositions (including gels) as opposed to a solid or a gas.

[0015] The liquid hard surface cleaning compositions are preferably aqueous compositions. Therefore, they may comprise from 70% to 99% by weight of the total composition of water, preferably from 75% to 95% and more preferably from 80% to 95%.

[0016] The compositions herein may have a water-like viscosity. By "water-like viscosity" it is meant herein a viscosity that is close to that of water. Preferably the liquid acidic hard surface cleaning compositions herein have a viscosity of up to 50 cps at 60rpm, more preferably from 1 cps to 30 cps, yet more preferably from 1 cps to 20 cps and most preferably from 1 cps to 10 cps at 60rpm and 20°C when measured with a Brookfield digital viscometer model DV II, with spindle 2. [0017] In other embodiments, the compositions can be thickened. Thus, the liquid hard surface cleaning compositions herein preferably have a viscosity of from 50 cps to 5000 cps at 10 s⁻¹, more preferably from 50 cps to 2000 cps, yet more preferably from 50 cps to 1000 cps and most preferably from 50 cps to 500 cps at 10 s⁻¹ and 20°C when measured with a Rheometer, model AR 1000 (Supplied by TA Instruments) with a 4 cm conic spindle in stainless steel, 2° angle (linear increment from 0.1 to 100 sec⁻¹ in max. 8 minutes). Preferably, the thickened compositions according to this specific embodiment are shear-thinning compositions. The thickened liquid acidic hard surface cleaning compositions herein preferably comprise a thickener, more preferably a polysaccharide polymer as thickener, still more preferably a gum-type polysaccharide polymer thickener and most preferably xanthan gum.

[0018] The compositions of use in the present invention comprise polyquaternium-95, which is a copolymer of corn starch, acrylic acid (or salts thereof) and acrylamido-propyl-methyl-ammonium chloride.

[0019] The composition preferably comprises polyquaternium-95 as the sole surface modification polymer. Alternatively, the composition can comprise additional surface modification polymers, such as those selected from the group consisting of: homopolymers of polyvinylpyrrolidone; copolymers of polyvinylpyrrolidone; polysulphobetaine polymers; copolymers of diallyldimethylammonium chloride and acrylic acid (or salts thereof); and mixtures thereof.

[0020] The polyquaternium-95 can have a weight average molecular weight of from 2,000 to 1,000,000 Da, preferably from 5,000 to 500,000 Da, more preferably from 10,000 to 300,000 Da.

[0021] The polyquaternium-95 can be present at a level of from 0.01% to 5%, preferably from 0.02% to 2%, more preferably from 0.05% to 1.0% by weight of the composition. If further surface modification polymers are present, the total level of surface modification polymer can be at a level of from 0.01% to 5%, preferably from 0.02% to 2%, more preferably from 0.05% to 1.0% by weight of the composition.

[0022] The surface modification polymers of use in the compositions of the present invention are generally provided as a mixture which includes the polymer dispersed in an aqueous or aqueous/alcoholic carrier.

[0023] Suitable vinylpyrrolidone homopolymers for use herein are homopolymers of N-vinylpyrrolidone. Suitable vinylpyrrolidone homopolymers can have a degree of polymerisation such that the weight average molecular weight of the homopolymer is from 1,000 to 100,000,000, preferably from 10,000 to 1,000,000, more preferably from 25,000 to 7,500,000, and most preferably from 300,000 to 500,000. Suitable vinylpyrrolidone homopolymers are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15® (viscosity molecular weight of 10,000), PVP K-30® (average molecular weight of 40,000), PVP K-60® (average molecular weight of 160,000), and PVP K-90® (average molecular weight of 360,000). Vinylpyrrolidone homopolymers are known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

[0024] Suitable vinylpyrrolidone copolymers are more fully described in United States Patent No. 4,445,521, United States Patent No. 4,165,367, United States Patent No. 4,223,009, United States Patent No. 3,954,960, as well as GB1331819. Suitable polyvinylpyrrolidone copolymers include vinylpyrrolidone / dimethylaminoethylmethacrylate (VP/DMAEMA) copolymers. Such copolymers can have a weight average molecular weight of from 50,000 to 5,000,000 Da, preferably 100,000 Da to 2,500,000Da, more preferably from 500,000 to 1,500,000 Da. Suitable polymers are available commercially, including from Ashland Inc. under the tradenames Sorez™ HS-205, copolymer 845, copolymer 937, copolymer 958. Suitable vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers are commercially available under the name copolymer 845®, Gafquat 734®, or Gafquat 755® from ISP Corporation, New York, NY and Montreal, Canada or from BASF under the tradename Luviquat®.

[0025] Suitable polysulphobetaine polymers comprise zwitterionic sulphobetaines monomers. The polysulphobetaine polymer can be a homopolymer or a copolymer comprising one or more of sulphobetaines monomers, though homopolymers are preferred. The betaine groups are typically the pendant groups of the polysulphobetaine polymer herein, typically obtained from monomers containing at least one ethylene unsaturation. The polysulphobetaine polymer herein

may have a molar mass going from 5,000 g/mol to 3,000,000 g/mol, preferably from 8,000 to 1,000,000 g/mol, more preferably from 10,000 to 500,000 g/mol. Suitable polysulphobetaine polymers are further described in EP2272942A1, particularly paragraph [0042] to [0085].

[0026] The compositions of the present invention can comprise surfactant. Preferred surfactants can be selected from the group consisting of: nonionic surfactant, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

[0027] Nonionic surfactants are particularly preferred. As such, the compositions of use in the present invention can comprise a nonionic surfactant, or a mixture thereof. This class of surfactants may be desired as it further contributes to cleaning performance of the hard surface cleaning compositions herein. It has been found in particular that nonionic surfactants strongly contribute in achieving highly improved performance on greasy soap scum removal.

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[0028] The compositions of use in the present invention may comprise up to 15% by weight of the total composition of a nonionic surfactant or a mixture thereof, preferably from 0.1% to 10%, more preferably from 0.5% to 5.0%, even more preferably from 1.0% to 3.0% by weight of the total composition.

[0029] Suitable nonionic surfactants for use herein are alkoxylated alcohol nonionic surfactants, which can be readily made by condensation processes which are well-known in the art. However, a great variety of such alkoxylated alcohols, especially ethoxylated and/or propoxylated alcohols, are conveniently commercially available. Surfactants catalogs are available which list a number of surfactants, including nonionics.

[0030] Preferred nonionic surfactants for use in the compositions according to the invention are the condensation product of ethylene and/or propylene oxide with an alcohol having a straight alkyl chain comprising from 6 to 22 carbon atoms, wherein the degree of ethoxylation/propoxylation is from 1 to 15, preferably from 5 to 12 or mixtures thereof. Such suitable nonionic surfactants are commercially available from Shell, for instance, under the trade name Neodol® or from BASF under the trade name Lutensol®, and from Sasol under the tradename Marilpal®.

[0031] Amine oxide surfactants are also suitable nonionic surfactants. Examples of amine oxides for use herein are for instance coconut dimethyl amine oxides, C12-C16 dimethyl amine oxides. Said amine oxides may be commercially available from Clariant, Stepan, and AKZO (under the trade name Aromox®).

[0032] In preferred embodiments, the composition comprises limited amounts, or no anionic surfactant. As such, the hard surface composition can comprise less than 2wt%, preferably less than 1wt%, more preferably less than 0.5wt%, most preferably less than 0.1% by weight of anionic surfactant.

[0033] Suitable anionic surfactants include alkyl sulphonates, alkyl aryl sulphonates, or mixtures thereof.

[0034] If used, suitable linear alkyl sulphonates include C8 sulphonate like Witconate® NAS 8 commercially available from Witco.

[0035] Suitable zwitterionic surfactants for use herein contain both basic and acidic groups which form an inner salt giving both cationic and anionic hydrophilic groups on the same molecule at a relatively wide range of pH's. The typical cationic group is a quaternary ammonium group, although other positively charged groups like phosphonium, imidazolium and sulphonium groups can be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used.

[0036] Some common examples of zwitterionic surfactants (i.e. betaine/sulphobetaine) are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082.

[0037] Amphoteric and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system are represented by detergents such as dodecylbetaalanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378. Additional synthetic detergents and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1980.

[0038] Cationic surfactants suitable for use in compositions of the present invention are those having a long-chain hydrocarbyl group. Examples of such cationic surfactants include the quaternary ammonium surfactants such as alkyld-imethylammonium halogenides. Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

[0039] The liquid compositions of the present invention are preferably acidic. Therefore the liquid hard surface cleaning composition of the present invention has a pH, measured on the neat composition, at 25°C, of less than 7.0, or from 1.5 to less than 7.0, preferably from 2.0 to 3.0, more preferably from 2.1 to 2.4.

[0040] The composition can comprise an organic acid system, for improved safety on delicate surfaces, including chromed surfaces and stainless steel surfaces. Typically, the acid system comprises any organic acid well-known to those skilled in the art, or a mixture thereof. The organic acid system can comprise acids selected from the group consisting of: citric acid, formic acid, acetic acid, maleic acid, lactic acid, glycolic acid, oxalic acid, succinic acid, glutaric acid, adipic acid, methansulphonic acid, and mixtures thereof, preferably acids selected from the group consisting of: citric acid, formic acid, acetic acid, and mixtures thereof.

[0041] The composition preferably comprises the acid system at a level of from 0.01 % to 15%, preferably from 0.5%

to 10%, more preferably from 2% to 8%, most preferably from 4% to 7.5% by weight of the total composition. The weight percentages are measured according to the added amounts of the acid, before any in-situ neutralization.

[0042] The compositions herein can comprise an alkaline material. The alkaline material may be present to trim the pH and/or maintain the pH of the compositions according to the present invention. Examples of alkaline material are sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such, as sodium and/or potassium oxide or mixtures thereof and/or monoethanolamine and/or triethanolamine. Other suitable bases include ammonia, ammonium carbonate, choline base, etc. Preferably, source of alkalinity is sodium hydroxide or potassium hydroxide, preferably sodium hydroxide.

[0043] Typically the amount of alkaline material is of from 0.001 % to 20 % by weight, preferably from 0.01 % to 10 % and more preferably from 0.05 % to 3 % by weight of the composition.

[0044] Despite the presence of alkaline material, if any, the compositions herein preferably remain acidic compositions.

[0045] The compositions according to the present invention may comprise a variety of optional ingredients depending on the technical benefit aimed for and the surface treated.

[0046] Suitable optional ingredients for use herein include other acids, chelating agents, polysaccharide polymer, radical scavengers, perfumes, solvents, other surfactants, builders, buffers, bactericides, hydrotropes, colorants, stabilizers, bleaches, bleach activators, suds controlling agents like fatty acids, enzymes, soil suspenders, brighteners, dispersants, pigments, and dyes.

The process of cleaning a hard-surface or an object

[0047] The hard surface cleaning compositions are used to provide prevention or reduction of water marks and splash marks. The compositions described herein are particularly suited for the prevention of water marks on inclined surfaces such as vertical surfaces.

[0048] The preferred process of cleaning a hard-surface or an object comprises the step of applying a composition according to the present invention onto the hard surface, leaving said composition on said surface, preferably for an effective amount of time, more preferably for a period comprised between 10 seconds and 10 minutes, most preferably for a period comprised between 15 seconds and 4 minutes; optionally wiping said hard-surface or object with an appropriate instrument, e.g. a sponge; and then preferably rinsing said surface with water.

[0049] The compositions of use in the present invention may be contacted to the surface to be treated in its neat form or in its diluted form. Preferably, the composition is applied in its neat form.

[0050] The compositions according to the present invention are particularly suitable for treating hard-surfaces located in and around the house, such as in bathrooms, toilets, garages, on driveways, basements, gardens, kitchens, etc., and preferably in bathrooms. Surfaces to be treated include ceramic surfaces (such as tiles and porcelain wear, including sinks, toilets and the like), glass surfaces (such as mirrors and glass shower walls), metal surfaces (such as brass, stainless steel and copper), other hard surfaces where splash marks are visible, as well as combinations thereof. The compositions described herein are particularly suited for treating ceramic surfaces.

[0051] The compositions herein may be packaged in any suitable container, such as bottles, preferably plastic bottles, optionally equipped with an electrical or manual trigger spray-head.

40 METHODS

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A) pH measurement:

[0052] The pH is measured on the neat composition, at 25°C, using a Sartorius PT-10P pH meter with gel-filled probe (such as the Toledo probe, part number 52 000 100), calibrated according to the instructions manual.

EXAMPLES

[0053] These following compositions were made comprising the listed ingredients in the listed proportions (active weight %). Example 1 was a composition of use in the present invention, while example A was comparative, comprising a sulphobetaines surface modification polymer. The relative amounts of splash marks after multicycle spraying and rinsing was evaluated using the following procedure:

Senio glossy black tiles were cleaned using a nil-polymer all-purpose cleaner and cellulose sponge before rinsing for 5 minutes under running water and drying with a paper towel. The tiles were then rinsed using isopropanol and dried using a paper towel.

[0054] A Hansgrohe Croma Variojet shower head, set to position "3" on the shower head, was connected to the coldwater mains supply and mounted in a horizontal position 115 cm above a shower basin, and 9 cm from the shower cabinet wall. The test tile was positioned on the wall, just above the shower basin. The water flow rate was set to 10L/min

and the shower turned on for 15 minutes before the tile was left to dry. The relative amounts of splash marks after spraying and rinsing three times (3 cycles) was evaluated using the following relative grading scale with the composition of comparative example A as reference, by two graders:

0 = there is no difference

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1 = I think there is a difference

2 = I am sure there is a difference

3 = there is a big difference

4 = there is a very big difference

[0055] The test was repeated to result in a total of 4 gradings, and the results averaged.

[0056] A higher grading indicates less splash marks versus the reference.

Composition	Ex 1	Ex A*
	wt%	wt%
Citric acid	1.7	1.7
Formic acid	2.7	2.7
C9-C11 8EO ¹	2.2	2.2
Xanthan gum	-	-
Perfume	0.2	0.2
dyes	0.008	0.008
Polyquaternium-95 ¹	0.1	-
Sulphobetaine polymer ²	-	0.5
Water	Balance up to 100	Balance up to 100
Sodium hydroxide	to pH 2.2	to pH 2.2
Splash marks (visual grading) after 3 cycles	+2.9	REF

As can be seen from the grading data above, the use of a hard surface cleaning composition comprising polyquaternium 95 results in improved water-mark and splash-mark prevention, even when used at levels 5 times less than the polymer of the comparative example.

[0057] Examples 2 to 10 are further examples of compositions of use in the present invention.

Examples:	2	3	4	5	6	7	8	9	10
Formic acid ¹	4.0	2.0	1.8	1.8	2.5	2.0	2.0	2.0	4.0
Acetic acid ¹	-	3.5	8.0	8.0	5.5	6.0	5.0	-	-
Citric acid ¹	-	-	-	-	-	-	-	8.0	2.0
Lactic acid ¹	-	-	-	1.0	2.0	-	1.0	-	1.5
C ₉ -C ₁₁ EO8 ²	2.0	4.0	2.2	5.0	3.0	5.0	2.5	2.0	1.8
Xanthan gum	-	0.25	0.25	0.25	0.25	0.10	0.30	0.20	0.25
Polyquaternium 95 ³	0.05	0.1	2.0	0.15	0.1	0.02	0.1	0.1	0.1
Sulphobetaine polymer ⁴	-	-		0.1	0.5	-	0.15	0.1	-

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(continued)

Examples:	2	3	4	5	6	7	8	9	10
polyvinyl pyrrolidine ⁵	-	-	0.1	-	-	0.2	-	-	-
Polyacrylic acid, Na-salt ⁶	-	-	0.1	0.05	-	0.2	-	0.1	0.1
n-BPP ⁷	1.0	-	-	-	2.0	-	-	-	-
Minors *	0.10	0.50	0.25	0.55	0.10	0.50	0.3	0.20	0.3
KOH - to pH:	2.3	ı	2.9	2.8	2.8	ı	-	-	1
NaOH - to pH:	i	2.2	ı	-	ı	2.5	2.3	2.0	2.2
Water	to 100%								

^{*} preservative, dye, perfume, etc.

[0058] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Claims

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- 1. The use of polyquaternium-95 in a hard surface cleaning composition to prevent or reduce water-marks or splash marks on the treated surface.
- 2. The use according to claim 1, wherein the composition comprises the polyquaternium-95 as a level of from 0.01 % to 5 %, preferably from 0.02 % to 2 %, more preferably from 0.05 % to 1.0 % by weight of the composition.
 - **3.** The use according to any preceding claim, wherein the polyquaternium-95 is the sole surface modification polymer in the hard surface cleaning composition.
- **4.** The use according to any preceding claim, wherein the hard surface cleaning composition comprises surfactant, preferably nonionic surfactant.
 - **5.** The use according to claim 4, wherein the hard surface cleaning composition comprises nonionic surfactant at a level of up to 15%, preferably from 0.1% to 10%, more preferably from 0.5% to 5.0%, even more preferably from 1.0% to 3.0% by weight of the total composition
 - **6.** The use according to any preceding claim, wherein the hard surface cleaning composition has a pH, measured on the neat composition, at 25°C, of less than 7.0, preferably from 1.5 to less than 7.0, more preferably from 2.0 to 3.0, most preferably from 2.1 to 2.4.
 - **7.** The use according to any preceding claim, wherein the treated surface is selected from: ceramic surfaces, glass surfaces, metal surfaces, and combinations thereof.

¹ Formic acid, lactic acid and acetic acid are commercially available from Aldrich

² Nonionic surfactant, sourced as Neodol® 91-8 from Shell.

³ copolymer of corn starch, acrylic acid (or salts thereof) and acrylamido-propyl-methyl-ammonium chloride, supplied as Polyquart Ecoclean® by BASF

⁴ Sulphobetaine polymer of example 1.1 of EP2272942 B1, supplied by Solvay

⁵ polyvinylpyrrolidone homopolymer, commercially available from ISP Corporation

⁶ Sokalan RO1000, sourced from BASF

⁷ n-BPP is commercially available as DOWANOL® DPnB from DOW

8. The use according to claim 7, wherein the treated surface is a ceramic surface.

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EUROPEAN SEARCH REPORT

Application Number

EP 18 17 2219

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