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(54) **A method of cleaning a substrate**

(57) The invention provides a method of cleaning a substrate comprising the steps of:
a. contacting at least 10 μg of C8-C30 fatty acid per cm^2 area of the substrate, and;
b. exposing the substrate to a radiation in ultraviolet, visible or infrared spectrum.

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Description

Technical Field

[0001] This invention relates to a method of cleaning a substrate. It particularly relates to a method of cleaning fabric, especially for removal of stain from fabric.

[0002] The invention has been developed primarily for method of cleaning fabrics and will be described hereinafter with reference to this application. However, it will be appreciated that the invention is not limited to this particular field of use.

Background and Prior Art

[0003] Stains are localized soils on the fabrics that typically stand out due to colour and appearance that is distinct from the rest of the fabric. One of the commonest form of stains are foodstains, generally caused by accidental spilling of food materials or by brushing of clothing items like necktie against a food item, or by contact of food-laden cutlery and/or hands with an item of clothing.

[0004] Food stains are typically due to condiments like chilli or turmeric and food accompaniments like tomato ketchup and mustard sauce etc. Food materials generally contain chromophoric materials such as curcumin, carotenoids (such as lycopene, β-carotene, and oleoresin) and the like, that give the food stains a characteristic bright colour. In most cases, food materials also include oily or fatty materials making it more difficult to wash the foodstains off with water. For example, pickles used in Asian eating habits, unlike the ones used in European or American pickles, typically contain oil, chilli powder and turmeric, and a layer of oil with bright yellow or reddish colour can be typically seen floating on top. There is also a high likelihood of the area stained with food material developing microbial contamination and/or unpleasant odour.

[0005] Often, the foodstains occur when the user does not have time or facility to clean, i.e. during traveling, during business meetings or during working hours. Even if there is time or facility to clean, the garment needs to be removed in order to clean the stain effectively, causing inconvenience.

[0006] Conventional methods of cleaning with detergents, soaps and the like are relatively less effective in removing food stains. Further, it is inconvenient and wasteful to clean entire garment which is otherwise clean except for a small stained area.

[0007] Therefore, approaches for localized cleaning of stains or spot cleaning have been explored in the past. Cleaning with bleaches or other oxidizing agents, though relatively easy and effective, is likely to cause damage to fabrics and/or hands.

[0008] The approach of using solvents such as acetone or chlorinated solvents such as perchloroethylene is fraught with safety and environmental concerns.

[0009] Method of removal of stains from a surface by contacting the surface with photocatalytic materials followed by exposure to ultraviolet, visible or infrared irradiations have therefore been explored in the past. US20050227557 A1 (Li, 2005) discloses a method of making fabric with a photocatalyst, and in particular a manufacturing method for applying the photocatalyst to a fabric, so that the fabric has functions of sterilizing, deodorizing, self-cleaning, and anti-mildew when exposed to light. It discloses a method of making fabric with photocatalyst comprising the following steps. A length of fabric is cleansed with a water solution, and the solution on the fabric is dehydrated to eliminate miscellaneous articles. A photocatalyst solution comprising titania powder, acetone, resin and water is applied to the fabric and surplus photocatalyst solution is eliminated, and the fabric is dried to solidify the photocatalyst on the fabric.

[0010] This method requires use of organic solvents like acetone and binders like resins in the photocatalyst solution for even application of the titania powder. Further, the photocatalyst solution contains about 75-96.9 % water by weight, which must be dried, a step which requires energy and time.

[0011] It is also known to use photosensitizers in combination with photocatalyst in cleaning compositions.

[0012] US7141125 (Reckitt Benckiser, 2006) discloses a photocatalytic composition for cleaning including a photocatalytic material and a photosensitizer, and a method of cleaning by applying a photocatalytic material and a photosensitizer at a locus, for example on a surface. The residue combats soils and/or undesired micro-organisms at the locus. The photocatalytic material is peroxo modified titania, preferably in its anatase form, or peroxo modified titanic acid, or a mixture thereof. The compositions are preferably alkaline.

[0013] The prior art methods using photocatalyst are relatively slow as these involve cleaning compositions comprising a relatively large amount of water which requires relatively long time for drying. In addition, such compositions comprising relatively large amount of water, if applied to a fabric that is being worn by a user, cause unpleasant and inconvenient wet sensation, besides sometime resulting into unwarranted spreading of stains to previously unstained portions of the fabric. Thus there is an unfulfilled need for a method for removing stain from a garment whilst the garment is being worn by the user. There is a further need for a method that is relatively quick as compared to prior art methods.

Objects of the Invention

[0014] It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

[0015] One of the objects of the present invention is to provide a relatively fast method of cleaning a substrate.

[0016] Another object of the present invention is to provide a method of cleaning a fabric.

[0017] Yet another object of the present invention is to provide a method of removing stains from the fabric.

[0018] Present inventors have surprisingly found that contacting a substrate with fatty acid and exposing the substrate to radiation results into faster and more convenient cleaning of the substrate.

Summary of the Invention

[0019] According to the present invention, there is provided a method for cleaning a localized stain from the fabric comprising the steps of:

a) contacting at least 10 μg of C8-C30 fatty acid per cm^2 area of the substrate, and;
b) exposing the substrate to a radiation in ultraviolet, visible or infrared spectrum.

[0020] According to another aspect of the present invention, there is provided a cleaning composition comprising from 70 to 99.99% by weight C8-C30 fatty acid and from 0.01 to 10% by weight a photocatalyst.

Detailed Description of the Invention

[0021] According to the present invention, there is provided a method for cleaning a substrate comprising the steps of:

a. contacting at least 10 μg of C8-C30 fatty acid per cm^2 area of the substrate, and;
b. exposing the substrate to a radiation in ultraviolet, visible or infrared spectrum.

Substrate

[0022] The substrate that can be cleaned using the method of the present invention includes a fabric as well as hard surface such as metal, plastic, glass and the like. The substrate is preferably fabric, more preferably a localized stained area of the fabric. When the method is used for cleaning localized stained area from a fabric, it is not necessary to contact the entire fabric with the fatty acid.

[0023] The term "area" as used herein means the apparent surface area of substrate that is in contact with the fatty acid. For example, a swatch of fabric of square shape with side equal to 10 cm has area of 100 cm^2.

Fatty acid

[0024] According to the present invention, fatty acid of chain length from 8 to 30, preferably from 10 to 22, and more preferably from 12 to 18 is contacted with the substrate.

[0025] The amount of the fatty acid contacted with the substrate is at least 10 μg per cm^2 area of the substrate.

[0026] The amount of the fatty acid is preferably from 10 to 5000 μg, more preferably from 40 to 3000 μg, and most preferably from 40 to 1000 μg per cm^2 area of the substrate contacted.

[0027] The fatty acid can be saturated or unsaturated. However, unsaturated fatty acid is preferred. Preferably, the iodine value of fatty acid is greater than 30, more preferably greater than 60, most preferably greater than 90.

[0028] Fatty acid can be in a solid or liquid form. It is preferred that the fatty acid used in the process of the present invention is liquid at room temperature.

[0029] The melting point of the fatty acid is preferably greater than 25 °C, more preferably greater than 20 °C and most preferably greater than 10 °C.

[0030] When a solid fatty acid is used, it is preferably to mix it with a non-aqueous liquid carrier. Suitable non-aqueous liquid carrier includes vegetable oil and C6-C10 alkanes.

Photocatalyst

[0031] The method of cleaning preferably comprises a step of contacting from 0.01 to 1 μg photocatalyst per cm^2 area of the substrate. The amount of photocatalyst is preferably from 0.01 to 0.1 μg, more preferably from 0.01 to 0.04μg per cm^2 area of the substrate.

[0032] The step of contacting the substrate with the photocatalyst is preferably concurrent with the step of contacting the substrate with C8-C24 fatty acid. It is further preferred that the fatty acid and the photocatalyst are mixed together prior to contacting with the substrate.

[0033] The photocatalyst is preferably selected from titanium dioxide, zinc oxide, stannic oxide, ferric oxide, tungsten trioxide, cadmium sulphide, cadmium selenide, zinc sulphide, or mixtures thereof.

[0034] It is particularly preferred that the photocatalyst is titanium dioxide. Titanium dioxide exists in anatase, rutile and brookite crystalline forms, and any one of the crystalline form of titanium dioxide can be used in the method of the present invention. It is also possible to use a mixture of titanium dioxide of various crystalline forms. It is particularly preferred that titanium dioxide is of anatase form.

Photosensitizer

[0035] The process of the present invention preferably comprises a step of contacting 0.005 to 0.1 μg photosensitizer per cm^2 area of the substrate. The amount of photosensitizer is preferably from 0.005 to 0.05 μg, more preferably from 0.005 to 0.02 μg per cm^2 area of the substrate.

[0036] The step of contacting the substrate with the photosensitizer is preferably concurrent with the step of contacting the substrate with the photocatalyst. The photocatalyst, the photosensitizer and the fatty acid are preferably mixed together prior to contacting with the substrate.

[0037] The term photosensitizer as used herein means a chemical compound that readily undergoes photoexcitation and then transfers its energy to other molecules, thus making the reaction mixture more sensitive to light. Any photosensitizer can be used in the present invention. Some non-limiting examples of photosensitizer include transition metal complexes (like ruthenium complexes), porphyrins, phthalocyanines, coumarin, carboxylated derivatives of anthracene, dyes and carbonyl compounds. It is particularly preferred that the photosensitizer is selected from porphyrin, methylene blue, Rose Bengal or benzophenone.

Water

[0038] Preferably, amount of water in contact with the substrate during the process is less than 20 mg water per cm^2 area of the substrate. It is particularly preferred that the substrate is not contacted with water during the process. When the substrate is a fabric, the weight ratio of water to fabric is preferably less than 5, more preferably less than 2, and most preferably less than 1. It is particularly preferred that the fabric is not contacted with water during the process. The benefit of not contacting the fabric with water is that the process can be used to remove a stain from a garment that is being worn by a user, without causing unpleasant and inconvenient wet sensation, or without resulting into unwarranted spreading of stains to previously unstained portions of the fabric. The photocatalyst can be easily dispersed in the liquid fatty acid, or a non-aqueous liquid carrier mixed with the fatty acid for uniform application on a substrate in absence of water, and therefore the problem of patchy or non-uniform cleaning associated with use of solid photocatalyst is obviated.

Solvent

[0039] The substrate may be contacted with an organic solvent during the process. Chlorinated as well as non-chlorinated solvents such as chloroform, acetone or perchloroethylene may be used. However, it is preferred that the substrate is not contacted with a solvent during the process.

Soap and detergent

[0040] The method of present invention may involve a step of contacting the substrate with soap or detergent. However, it is preferred that the substrate is not contacted with soap or detergent during the process. The substrate may be washed with a cleaning composition comprising soap or detergent after or prior to the process of the present invention.

Radiation

[0041] The process of the present invention includes a step of exposing the substrate to a radiation in ultraviolet, visible or infrared spectrum, after the step of contacting the substrate with fatty acid.

[0042] Preferably, the radiation has a wavelength from 200 nm to 10000 nm. Source of radiation that can be used includes uv-lamps, infrared lamps, fluorescent or incandescent lights, and sunlight. It is particularly preferred that the substrate is exposed to sunlight.

Cleaning composition and forms

[0043] According to an aspect of the present invention, there is provided a cleaning composition comprising from 70 to 99.99% by weight C8-C30 fatty acid and from 0.01 to 10% by weight a photocatalyst.

[0044] According to a further preferred aspect, the cleaning composition further comprises from 0.01 to 5% by weight a photosensitizer.

[0045] It is envisaged that the cleaning composition according to the present invention can be used in any format that is convenient for contacting with the substrate. The cleaning composition may be in form of solid, liquid, paste or a gel.

[0046] The solid cleaning composition is preferably in the form of powder, granules, or a rigid abradable stick that can be conveniently contacted with a substrate. The cleaning composition in stick format may comprise particulate filler material and binder materials.

[0047] The liquid cleaning composition is packaged preferably in a form that allows easy dispensing, more preferably in a form that allows directed spraying of the liquid cleaning composition on a substrate. The dispensing or spraying may be actuated by mechanical action such as squeezing of a flexible packaging or by operating a piston pump. Alternatively, the liquid cleaning composition may be packaged along with a propellant carrier such as butane and stored in a pressurized container that allows spraying of the liquid composition on the substrate.

[0048] The cleaning composition may be in form of a gel or a paste and packaged in squeeze-tubes for easy dispensing.

Additional advantages of the process

[0049] The method for cleaning can be conveniently used to remove stains from a garment whilst the garment is being worn by the user.

[0050] The method of the present invention provides an advantage of relative reduction in malodour from a substrate.

[0051] The method of the present invention provides an advantage of relative reduction in bacterial contamination of the substrate.

[0052] According to one aspect, the method offers benefit in cleaning a plastic substrate. In particular, plastic food containers that have been tinged yellowish over period of time, and which are difficult to clean by prior art methods, can be conveniently and relatively quickly cleaned using the process of the present invention.

Examples

[0053] The invention will now be illustrated by way of examples. The examples are for the purpose of illustration only and do not limit the scope of the invention in any manner.

[0054] Materials used in the examples are given below in Table 1:

Table 1 : Materials

Material (chemical name and trade name, if any)	Source
P25® - Titanium dioxide	Degussa
Oleic acid	SD fine Chemicals
Isostearic acid	Fluka Chemicals
Mineral oil, Light white oil	Sigma
SAFAL® - Sunflower Oil	Karnataka co-op Oilseeds Growers Federation Ltd.
Cobalt tetra phenyl porphyrin complex	Aldrich Chem Co.
SURF EXCEL®	Hindustan Unilever Limited
White cotton fabric	Bombay Dyeing
Lemon Pickle	MTR®
Red Chilli Powder	Grocery shop
Acetone (GR Grade)	Merck

Preparation of stained fabric swatches

Preparation of swatches prior to staining

[0055] 100% pure cotton white fabrics (ex Bombay Dyeing, India) were used in all the stain degradation experiments. Prior to staining, they were washed five times and then ironed. Washing was carried out in a top loading washing machine (Whirlpool) using a commercial detergent, SURF EXCEL®. The washing protocol involved soaking the fabrics in SURF EXCEL® at 3 g/L dosage (with the ratio of mass of liquid to the mass of fabric, or the liquor to cloth ratio being approximately equal to 15) for 15 minutes followed by a wash for 30 min and then by two rinses.

Preparation of Oleoresin extract

[0056] Oleoresin was extracted from red chilli powder using acetone. The extraction was carried out till the residue became colourless. The residue was removed from the extract by centrifugation. All the extracts were pooled together and the acetone was evaporated using a rota evaporator to give a dark red gummy oleoresin. 200 μl Oleoresin extract was dissolved in 5 ml of sunflower oil (SAFAL®), and this mix was used as a staining solution.

Staining of fabric swatches

Pickle stains

[0057] 20 μL of the oil floating on top of the MTR® lemon pickle (pickle oil) was loaded on to a 3.5 x 5.5 cm^2 cotton fabric. The stain was allowed to spread on the fabric for 5-10 minutes before carrying out stain degradation experiments. The stain was circular in all cases and the area was determined to be about 4.5 cm^2.

Oleoresin stains

[0058] The procedure given above for pickle stains was used except that 20 μL of oleoresin staining solution was used instead of pickle oil.

Method of cleaning stains

[0059] Fatty acids were used for cleaning. Also, various cleaning compositions with or without photocatalyst (P25®), with or without photosensitizer (Cobalt tetra phenyl porphyrin complex, and fatty acid (either oleic or stearic acid), were made by mixing the ingredients. Stained fabric swatches were contacted with the relevant composition by pipetting out requisite amount on the fabric, and spreading with a glass rod, if required. The fabric was then exposed to radiation in the solar light simulator (ATLAS CPS, intensity = 3.9 mW/cm^2) in all the experiments, unless specified otherwise. In some experiments, the step of exposure to radiation was eliminated and fabric swatches were stored in dark at ambient temperature (between 20 to 30 °C).

Evaluation of cleaning efficacy and cleaning speed

[0060] The stain on the exposed fabrics was extracted at regular time intervals with 12 ml of acetone and the absorbance of extract was measured at 450 nm. Stain from area of fabric unexposed to radiation was extracted with acetone and resulting extract was used to determine the initial absorbance, A_0. From the initial absorbance, A_0 and the absorbance after t minutes of exposure, At, the percentage of stain remaining on fabric was quantified using the following equation:

$$\% \text{ stain remaining} = (A_t \times 100)/A_0$$

When At equalled zero, the stained area appeared to be visually clean. The time required for A_t to equal zero, i.e. time required for complete degradation of the stain, was used as a measure of speed of the cleaning process.

Contacting with fatty acid and exposing to radiation

[0061] The process according to the present invention was used in Example 1. Stained fabric swatches prepared according to the method of staining described earlier were used in the experiments. The processes of comparative

examples 1-A and 1-B were outside the scope of the present invention. The details are given in Table 2.

Table 2 Contacting with fatty acid and exposing to radiation

Example No	Amount of isostearic acid contacted with fabric ($\mu g/cm^2$)	Exposure to radiation	Time for complete degradation of oleoresin stain	Time for complete degradation of pickle stain
1	50	Yes	25 min	25 min
1-A	50	No	> 2 days	> 2 days
1-B	No	Yes	60 min	30 min

[0062] The time required for complete stain degradation is also tabulated in Table 2 above. It is clear that the process of the present invention results in faster cleaning of both oleoresin and pickle stains.

Effect of type of fatty acid on cleaning speed

[0063] Oleic acid, an unsaturated fatty acid (iodine value of 85-90) was used in Example 2 whilst isostearic acid, a saturated fatty acid (iodine value of 0) was used in Example 3. The details and the resulting cleaning speeds are tabulated in Table 3 below.

Table 3: Effect of degree of saturation of fatty acid on cleaning speed

Ex No	Fatty acid and amount contacted with fabric ($\mu g/cm^2$)	Iodine value of fatty acid used	Time for complete degradation of oleoresin stain (min)	Time for complete degradation of pickle stain (min)
2	Oleic acid, 50	85-90	20	20
3	Isostearic acid, 50	0	25	25

[0064] The above results demonstrate that unsaturated fatty acid provides faster cleaning as compared to saturated fatty acid.

Effect of photocatalyst and amount of photocatalyst

[0065] In the process of Examples 4-7, stain is contacted with compositions comprising fatty acid and a photocatalyst. In the process of Comparative Example 7-A, photocatalyst is used in absence of fatty acid. In the process of Comparative Example 7-B, photocatalyst is used in combination with water instead of fatty acid. The details are given in Table 4.

Table 4: Effect of photocatalyst and amount of photocatalyst

Example No	Substance contacted with fabric and its amount ($\mu g/cm2$)	Time for complete degradation of pickle stain (min)
4	Isostearic acid (50) + P25® (0.044)	20
5	Oleic acid (50) + P25® (0.013)	15
6	Oleic acid (50) + P25® (0.027)	10
7	Oleic acid (50) + P25® (0.044)	5
7-A	P25® (0.044)	*
7-B	P25® (0.044) + water (50)	45
* Patchy or incomplete cleaning at 20 minutes		

[0066] Comparison of cleaning speed of Example 4 with Example 3 (results in Table 3), and Examples 5-7 with Example 2 (results in Table 3) clearly demonstrates that cleaning speed is enhanced by contacting the fabric with a photocatalyst. Examples 5-7 indicate that cleaning is quicker as the amount of photocatalyst contacted with the stain is increased. The process of Comparative Example 7-A results into patchy cleaning. Without wishing to be limited by theory,

it is believed that patchy cleaning that is observed is due to the difficulty in uniformly applying the solid photocatalyst powder on the stain. If the photocatalyst powder is dispersed in water to aid in uniform application, as in the process of Comparative Example 7-B, the cleaning is slower.

Effect of amount of fatty acid

[0067] Examples 7-9 show the effect of amount of fatty acid contacted. Example 7 is reproduced from Table 4 for convenience.

Table 5: Effect of amount of fatty acid

Example No	Substance contacted with fabric and its amount (μg/cm2)	Time for complete degradation of pickle stain (min)
8	oleic acid (10) + P25® (0.044)	15
9	oleic acid (20) + P25® (0.044)	10
7	oleic acid (50) + P25® (0.044)	5

[0068] The results indicate that the speed of cleaning is increased with the amount of fatty acid contacted with the stain.

Effect of photosensitizer

[0069] In the process of Example 10, the stain is contacted with a composition comprising fatty acid, photocatalyst and a photosensitizer. The composition used in the process of Example 7 is similar to that used in Example 10, except that it does not comprise a photosensitizer. The details are given in Table 6. Example 7 is reproduced from Table 4 for convenience.

Table 6: Effect of photosensitizer

Example No	Substance contacted with fabric and its amount (μg/cm2)	Time for complete degradation of pickle stain (min)
7	Oleic acid (50) + P25® (0.044)	5
10	Oleic acid (50) + P25® (0.044) + cobalt tetra phenyl porphyrin complex (0.02)	3

[0070] The results demonstrate the beneficial effect of addition of photosensitizer on the speed of cleaning.

[0071] It will be appreciated that the examples clearly show the mode in which the process of the present invention can be practiced. The examples also clearly demonstrate that the process of the present invention is relatively quick and convenient process for cleaning a substrate, particularly for stain removal from a fabric.

Claims

1. A method of cleaning a substrate comprising the steps of:

a. contacting at least 10 μg of C8-C30 fatty acid per cm^2 area of the substrate, and;
b. exposing the substrate to a radiation in ultraviolet, visible or infrared spectrum.

2. A method as claimed in claim 1 wherein said acid is unsaturated fatty acid.

3. A method as claimed in any one of the preceding claims wherein source of said radiation is sunlight.

4. A method as claimed in any one of the preceding claims comprising a step of contacting from 0.01 to 1 μg photocatalyst per cm^2 area of the substrate.

5. A method as claimed in claim 4 wherein said photocatalyst is titanium dioxide.

6. A method as claimed in claim 5 wherein said titanium dioxide is of anatase form.

7. A method as claimed in any one of the preceding claims comprising a step of contacting from 0.005 to 0.1 μg photosensitizer per cm^2 area of the substrate.

8. A cleaning composition comprising from 70 to 99.99% by weight C8-C30 fatty acid and from 0.01 to 10% by weight a photocatalyst.

9. A cleaning composition as claimed in claim 8 comprising from 0.01 to 5% by weight a photosensitizer.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 11 9609

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	16 April 2008	Péntek, Eric

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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