METHOD FOR RECONDITIONING THE SURFACE OF PLASTICS

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9 Claims

ABSTRACT OF THE DISCLOSURE

A method for reconditioning the stained or discolored surfaces of plastic objects to substantially restore them to their original condition which comprises the steps of treating the surface of a plastic object with an aqueous solution of chlorine-containing bleaching agent having a pH of more than 5, then treating the surface thereof with an aqueous solution of sulfur-containing bleaching agent having a pH of more than 5, and thereafter rinsing the surface with water.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 785,784, filed Dec. 20, 1968, now abandoned.

BACKGROUND OF THE INVENTION

(a) Field of the invention

The present invention relates to a method for reconditioning the surfaces of plastic objects in which a chlorine-containing bleaching agent and a sulfur-containing bleaching agent are employed for cleaning the stained or discolored surface of the plastic objects.

(b) Description of the prior art

Of late, there has been a marked increase in the demand for plastic tableware at such places as hospitals, schools, offices, factories, youth-hostels and so forth where mass feeding is carried out. Plastic tableware has many advantages such as durability, lightness and low cost. However, it has the drawback that the entire surface — especially the inner surface — of same is apt to become discolored gradually to a yellowish brown or blackish color when it is used for a long period of time. The stain or discoloration cannot be removed by ordinary prior art detergents. Particularly in the case of white-colored plastics, such stains or discolorations are even more pronounced and make the tableware look very unsightly, so that especially such facilities as hospitals and the like are often obliged to throw away such stained or discolored plastic tableware. This represents a great deal of economic loss.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method for reconditioning the surface of plastic objects by removing stains and/or discolorations, in which the stained or discolored surface of the plastic object is first treated with an aqueous solution of chlorine-containing bleaching agent, then treated with an aqueous solution of sulfur-containing bleaching agent, and lastly rinsed with water, thereby easily restoring the original cleanliness of the surface of the plastic object.

The aforesaid stains or discolorations of the surface of plastic objects are not the result of dirt or grime adhered temporarily onto said surface, but rather are caused by the degeneration of said surface due to repeated cleaning with detergents over a long period of time. Consequently, the thus stained or discolored surface of plastic objects can not be reconditioned with conventional detergents. As an alternative, the employment of such bleaching agents as sodium hypochlorite, sodium dichromate and the like is readily thought of. However, although the employment of these bleaching agents may be slightly effective in cleaning the stained or discolored surface of plastic objects, it is impossible to recondition them to the same cleanliness as that of a brand-new object. Surprisingly, it has been found that, when a chlorine-containing bleaching agent like sodium hypochlorite is first employed for cleaning said plastic objects and next a sulfur-containing bleaching agent like sodium dichromate is employed for cleaning same, the stained or discolored surface thereof is surprisingly restored to its original state. Another surprising finding is that, when such a bleaching agent like sodium dichromate is first employed and then a chlorine-containing bleaching agent like sodium hypochlorite is employed for cleaning purpose, the original cleanliness of the plastic object cannot be restored, and the effect of the cleaning is no better than in case of cleanings with only the sulfur-containing bleaching agent. The present invention is based on the above-stated discoveries.

As the chlorine-containing bleaching agent to be employed in the present invention, there can be used alkali metal hypochlorites and alkali metal chlorosocyanates. Sodium, potassium and lithium are the preferred alkali metals.

As the sulfur-containing bleaching agent to be employed in the present invention, there can be used alkali metal dichromates, alkali metal formaldehyde sulfoxylates, alkali metal sulfites and alkali metal hydrogen sulfites. Sodium, potassium and lithium are the preferred alkali metals.

The aqueous solution of the chlorine-containing bleaching agent should have a pH of more than 5. The concentration thereof, in terms of available chlorine, is required to be more than 100 p.p.m., and it is preferably within the range of 300-500 p.p.m. for practical use. If the chlorine concentration is less than 100 p.p.m. no appreciable reconditioning effect will be obtained, while an excessively high chlorine concentration will not necessarily bring about any corresponding improvement of the reconditioning effect. The higher is the temperature for the reconditioning process, the shorter will be the time required for the reconditioning process, but, in practice, it is preferred to operate within the range of 40°-60° C. Blending or mixing of sulfur-containing bleaching agent with said aqueous chloronic solution should be avoided, but no trouble will be caused by adding thereto other substances which do not reduce the bleaching ability of said aqueous chloronic solution—for instance, inorganic salts, such as sodium chloride. However, it is ordinarily unnecessary to add such substances to said aqueous chloronic solution. Moreover, it is unnecessary to exercise special care to avoid the presence of a small amount of detergent in said aqueous chloronic solution. Indeed it may be advisable to add a small quantity of detergent to said chloronic solution so that it may become capable of cleaning soil or grime and simultaneously to restore the cleanliness of the surface by removing stains or discolorations. Even in the latter case, however, the treatment with the sulfur-containing bleaching agent must be conducted subsequently. In other cases, it may be undesirable to use the chlorine-containing bleaching agent and a detergent simultaneously, because they may interact with a consequent reduction in their respective cleaning and bleaching efficiency.

The aqueous solution of the sulfur-containing bleaching agent should have a pH of more than 5. The concentration of the sulfur-containing bleaching agent is within the range of 0.5-2.0 wt. percent, preferably about 1 wt. percent, based on the weight of the solution.
higher is the temperature for the sulfuric bleaching process, the shorter will be the time required for the process. But, in practice, it is preferred to operate within the range of 60°–65°C. Mixing of detergents into said aqueous sulfuric bleaching solution should be avoided, but no harm will result from mixing therein some chlorine-containing bleaching agent, which is apt to occur during the course of processing, or by adding thereto some other substances which will not substantially reduce the bleaching ability of said aqueous sulfur-containing bleaching solution—such inorganic salts such as sodium sulfate. However, it is preferred not to add any additional substances for the sake of bleaching efficiency.

Furthermore, the plastic moldings are contacted with the respective aqueous solutions in the aforementioned order. Such methods as immersing, coating or spraying each aqueous solution onto the surface of plastic objects to be treated or combinations of these methods can be adopted. The coating method is carried out by employing, for instance, sponge, sprayer, cloth, brush, and so forth. Additionally, in the practice of the present invention, the time of contact between the plastic objects and the respective aqueous bleaching agent solutions, either chlorinatic or sulfuric, is preferably less than about 10 minutes, and more preferably less than 5 minutes. This is because some phenomena, such as fading, are liable to occur on the surface of the plastic objects if the contact time is longer.

The method according to the present invention is applicable to general plastic moldings such as tabletop, kitchen utensils, dish pans, toys, furniture, and so forth, which are made of a variety of resins, such as urea-formaldehyde resin, melamine-formaldehyde resin, phenol resin, polycarbonate, acrylonitrile-styrene copolymer (AS resin), acrylonitrile-butadiene-styrene copolymer (ABS resin), polyethylene, polypropylene, polystyrene, unsaturated polyester, polycarbonate and polyethylene terephthalate. In this connection, the unsaturated polyester includes one prepared by polycondensing unsaturated polybasic acid such as maleic acid, phthalic acid or isophthalic acid with polyl such as ethylene glycol, diethylene glycol, propylene glycol or glycerol and then vinyl-polymerizing the resulting copolymer with a polymerizable monomer, as a crosslinking agent, such as styrene or methylstyrene. The polycarbonate and the polyethylene terephthalate each are one made by subjecting to polymerization or copolymerization of at least one monomer represented by the formula \( CH_2=\text{C(R)}-\text{COOR' (wherein, in the case of polycarbonate, \( R \) and \( R' \) presents H and \( R \) presents alkyl such as methyl, ethyl, butyl, isobutyl and the like, and wherein, in the case of polyethylene terephthalate, \( R \) presents methyl and \( R' \) does the same as above defined.}

The method according to this invention is especially advantageous for reconditioning tableware.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Methods according to the present invention are disclosed in the following illustrative, non-limiting examples.

**Example 1**

Aqueous solutions of the following bleaching agents

1. (A) Sodium hypochlorite, 1% (available chlorine: 500 p.p.m.) aqueous solution
2. (B) Sodium hypochlorite, 2% (available chlorine: 1,000 p.p.m.) aqueous solution
3. (C) Sodium dichloroisocyanurate, 0.1% (available chlorine: 600 p.p.m.) aqueous solution
4. (D) Lithium hypochlorite, 1% (available chlorine: 500 p.p.m.) aqueous solution
5. (E) Sodium dithionite, 1% aqueous solution
6. (F) Sodium dithionite, 2% aqueous solution
7. (G) Sodium formaldehyde sulfoxylate, 1% aqueous solution
8. (H) Hydrogen peroxide, 1% aqueous solution

Next, 44 test plates (white-colored tableware made from urea-formaldehyde resin and approximately 20 cm. in diameter)—which had become blackish after being used for meals for a period of about one month—were picked up by a random sampling method. The plates had been cleansed with the usual detergents after each meal in the past. Prior to the experiment, the degree of stain or discoloration of said test plates in terms of reflectance was determined by means of a photo-electric reflectance-meter (manufactured by Hitachi Ltd., Japan). The reflectances thus measured averaged 15.86%. For the sake of comparison, 4 brand-new plates of the same kind as the aforesaid test plates were also tested in the same way to measure the reflectance thereof. The reflectances measured in this case averaged 80.3%.

The 44 test plates were divided into 11 groups—each group consisting of 4 plates, and the respective groups were treated as shown in the following table. Some groups were immersed in the 1st aqueous solution bath for about 1 min. and then taken out of it and then immersed in the 2nd aqueous solution bath for about 1 min. Then, said groups were taken out of the 2nd aqueous solution bath and were rinsed with flowing warm water and dried in the air. The other groups were immersed only into the 1st aqueous solution bath and taken out of it and were rinsed immediately. The temperature of said aqueous solution baths was adjusted to be 50°±2°C, in case of the aqueous solution of bleaching agent containing chlorine as well as hydrogen peroxide solution, and 70°±2°C in case of the aqueous solution of bleaching agent containing sulfur.

**EXAMPLE 2**

In this case, 4 test plates of the same kind as that employed in Example 1 were used. Said test plates were first sprayed with a 1 wt. percent-aqueous solution (available chlorine: 407 p.p.m.) (temperature: 55° C.) of potassium hypochlorite and left standing for 5 minutes. Following that, they were sprayed with a 1 wt. percent-aqueous solution (temperature: 70°C) of potassium dichloroammonium with left standing for 3 minutes. The plates thus treated were then rinsed and dried. The resultant reflectances of said plates averaged 78.0%.

**EXAMPLE 3**

There were treated three samples of tableware made of melamine-formaldehyde resin (manufactured by Fuji Kasel K.K. and marketed under the trade name "U-Con Melamine AM{}^{*}"), which had been used in a restaurant for about 6 months and had become dark. A warm aqueous solution (temperature: 50°C) containing 0.5 wt. percent potassium hypochlorite (available chlorine: 200 p.p.m.) was applied onto the samples and wiped off gently after 5 minutes. Subsequently, a warm aqueous solution (temperature: 70°C) containing 2 wt. percent of sodium dithionite was applied onto the thus treated samples and left standing for 1 minute. After that, the samples were
thoroughly rinsed with water and dried. The results of the treatment are indicated in the following table.

**EXAMPLE 4**

There were treated three samples of kitchen utensiles made of phenol resin (manufactured by Asahi Yukikogyo K.K. and marketed under the trade name “Av-Lite PM-GM #55”), which had been used in an office for 12 months and had become dark. A warm aqueous solution (temperature: 40° C.) containing 0.5 wt. percent of sodium hypochlorite (available chlorine: 250 p.p.m.) was sprayed onto the samples and wiped off gently after 10 minutes. Subsequently, a warm aqueous solution (temperature: 60° C.) containing 1 wt. percent of sodium formaldehyde sulfoxylate was sprayed onto the thus treated samples and left standing for 5 minutes. After that, the samples were thoroughly rinsed with water and dried. The results of the treatment are indicated in the following table.

**EXAMPLE 5**

There were treated two samples of plastic dish pans made of unsaturated polyester resin (manufactured by Hitachi Kasei K.K. and marketed under the trade name “Polyset 6664”), which had been used for domestic use for about 2 years and became yellowish and blackish. A warm aqueous solution (temperature: 40° C.) containing 0.2 wt. percent of potassium dichloroisocyanurate (available chlorine: 1200 p.p.m.) was sprayed onto the samples and wiped off gently after 5 minutes. Subsequently, a warm aqueous solution (temperature: 70° C.) containing 0.3 wt. percent of sodium hydrosulfite was sprayed onto the thus treated samples and left standing for 1 minute. After that, the samples were thoroughly rinsed with water and dried. The results of the treatment are indicated in the following table.

**EXAMPLE 6**

There were treated ten samples of table wares made of acryliclonitrile-styrene-butadiene (ABS) resin (manufactured by Ube Saikon K.K. and marketed under the trade name “Saikolac X–27”), which had been used for catering for about 6 months and became dark. These samples were first dipped in a warm aqueous solution (temperature: 50° C.) containing 1 wt. percent of lithium hypochlorite (available chlorine: 500 p.p.m.) for 5 minutes, and next dipped in a warm aqueous solution (temperature: 70° C.) containing 3 wt. percent of sodium hydrosulfite for 10 minutes. Subsequently, the thus treated samples were thoroughly rinsed with water and dried thereafter. The results of the treatment are indicated in the following table.

**Example 7**

There were treated four samples of toys made of polyethylene resin (manufactured by Mitsubishi Yuka K.K. and marketed under the trade name “Yukalon MS–70”), which had been used in homes for 12 months and became dark. These samples were first dipped in a warm aqueous solution (temperature: 40° C.) containing 1 wt. percent of sodium hypochlorite (available chlorine: 500 p.p.m.) for 1 minute, and next dipped in an aqueous solution (temperature: 60° C.) containing 0.5 wt. percent of sodium hydrosulfite for 1 minute. Subsequently, the thus treated samples were thoroughly rinsed with water and dried thereafter. The results of the treatment are indicated in the following table.

**Example 8**

There were treated four samples of receptacles made of polypropylene resin (manufactured by Mitsubishi Yuka K.K. and marketed under the trade name “Mitsubishi Noblen BC–8”), which had been used for domestic purposes for about 12 months and became dark. These samples were first dipped in a warm aqueous solution (temperature: 50° C.) containing 0.5 wt. percent of potassium dichloroisocyanurate (available chlorine: 300 p.p.m.) for 5 minutes, and next dipped in a warm aqueous solution (temperature: 70° C.) containing 1 wt. percent of potassium dichloroisocyanurate for 5 minutes. Subsequently, the thus treated samples were thoroughly rinsed with water and dried thereafter. The results of the treatment are indicated in the following table.

**Example 9**

There were treated two samples of stationery made of polystyrene resin (manufactured by Mitsubishi Monsanto Kasei K.K. and marketed under the trade name “Diarex Hiheat 102”), which had been used for domestic purposes for about 2 years and became dark. These samples were first dipped in a warm aqueous solution (temperature: 40° C.) containing 1 wt. percent of potassium hypochlorite (available chlorine: 400 p.p.m.) for 8 minutes, and next dipped in a warm aqueous solution (temperature: 60° C.) containing 2 wt. percent of sodium formaldehyde sulfoxylate for 1 minute. Subsequently, the thus treated samples were thoroughly rinsed with water and dried thereafter. The results of the treatment are indicated in the following table.

**Example 10**

There were treated two samples of chairs made of polyvinylchloride resin (manufactured by Mitsubishi Rayon K.K. and marketed under the trade name “Acrine VH”), which had been used in an office for about 2 years and became dark. A warm aqueous solution (temperature: 40° C.) containing 0.02 wt. percent of potassium dichloroisocyanurate (available chlorine: 1200 p.p.m) was applied onto these samples and wiped off gently after leaving it standing for 1 minute. Subsequently, a warm aqueous solution (temperature: 60° C.) containing 0.5 wt. percent of potassium formaldetlyde sulfoxylate was applied onto the thus treated samples and left standing for 1 minute. After that, the samples were thoroughly rinsed with water and dried. The results of the treatment are indicated in the following table.

**Example 11**

There were treated five samples of tableware made of polycarbonate resin (manufactured by Mitsubishi Edogawa Kagaku K.K. and marketed under the trade name “Eupiron E–1000”), which had been used in a restaurant for about 12 months and became dark. These samples were first dipped in a warm aqueous solution (temperature: 50° C.) containing 0.8 wt. percent of lithium hypochlorite (available chlorine: 400 p.p.m) for 5 minutes, and next dipped in a warm aqueous solution (temperature: 70° C.) containing 2 wt. percent of sodium dichloroisocyanurate for 2 minutes. Subsequently, the thus treated samples were thoroughly rinsed with water and dried thereafter. The results of these treatment are indicated in the following table.

<table>
<thead>
<tr>
<th>No. of example</th>
<th>Reflectance of articles before treatment</th>
<th>Reflectance of articles after treatment</th>
<th>Reflectance of brand-new articles</th>
<th>Regeneration rate, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42</td>
<td>60</td>
<td>62</td>
<td>90</td>
</tr>
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<tr>
<td>10</td>
<td>42</td>
<td>88</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>

*The treated articles were transparent, and, therefore, the measurement of the reflectance was performed by superposing the subject resin on an article on a blank paper envelope showing the same reflectance as a white standard plate.

What I claim is:

1. A method of reconditioning the surfaces of molded plastic tableware, comprising the steps of:
   applying to the surface of molded plastic tableware article made from a resin selected from the group consisting of urea-formaldehyde resin, melamine-formaldehyde resin, phenol resin, polycarbonate,
7 acrylonitrile-styrene copolymer, acrylonitrile-butadiene-styrene copolymer, polyethylene, polypropylene, polystyrene, unsaturated polyester, polyacrylate and polymethacrylate, a first treating solution at a temperature in the range of from 40° to 60° C., said first treating solution consisting essentially of an aqueous solution of chlorine-containing bleaching agent having a pH of more than 5 and containing more than 100 p.p.m. of available chlorine, said chlorine-containing bleaching agent being at least one member selected from the group consisting of alkali metal hypochlorites and alkali metal chloroisocyanurates; removing the tableware from contact with the first treating solution and then separately applying to the thus treated surface a second treating solution at a temperature between 60° C. and 80° C., said second treating solution consisting essentially of an aqueous solution of sulfur-containing bleaching agent having a pH of more than 5 and having a concentration of sulfur-containing bleaching agent in the range of 0.5–2.0 wt. percent, said sulfur-containing bleaching agent being at least one member selected from the group consisting of alkali metal dithionites, alkali metal formaldehyde sulfites, alkali metal sulfites and alkali metal hydrogen sulfites; and thereafter rinsing the surface of the plastic tableware with water and drying same.

2. A method according to claim 1, in which the available chlorine contained in said aqueous solution of the chlorine-containing bleaching agent is within the range

of 300–500 p.p.m., and the concentration of said aqueous solution of the sulfur-containing bleaching agent is about 1 wt. percent.

3. A method according to claim 1, wherein the article is made of melanine-formaldehyde resin.

4. A method according to claim 1, wherein the article is made of unsaturated polyester.

5. A method according to claim 1, wherein the article is made of acrylonitrile-butadiene-styrene copolymer.

6. A method according to claim 1, wherein the article is made of polypropylene.

7. A method according to claim 1, wherein the article is made of phenol resin.

8. A method according to claim 1, wherein the aqueous solution of the chlorine-containing bleaching agent and the aqueous solution of the sulfur-containing bleaching agent are each contacted with said article for a time period of less than about 10 minutes.

9. A method according to claim 8, wherein each contact time is less than about 5 minutes.

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