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(54) Title: SURFACE TREATMENT OF CERAMICS

(57) Abstract: A method of applying a silane-based surface coating to ceramic tableware is disclosed so as to improve the resistance of the surface of ceramic tableware to physical and chemical damage. The method includes the following steps: (i) Hydrating the surface of the ceramic tableware being treated; (ii) Removing substantially all dust from the ceramic tableware being treated; (iii) Applying a silane-based surface coating solution to the ceramic tableware being treated; (iv) Allowing the silane-based surface coating solution to cure on the ceramic tableware being treated; and (v) Heating the ceramic tableware being treated to a temperature sufficient to remove uncured silane-based surface coating solution from the ceramic tableware being treated.

Description

SURFACE TREATMENT OF CERAMICS

- [1] This invention relates to treating the finished surface of ceramics and in particular ceramic tableware to improve its properties.
- [2] Ceramic tableware such as plates, bowls, mugs, cups, serving dishes and similar articles are subjected in use or service to very demanding conditions of use which can lead to damage. Such damage may include mechanical damage such as chipping, cracking, breakage or scratching, and surface damage such as etching, discolouration, staining and marking. Such surface damage can be caused by prolonged or regular contact with highly alkaline detergent solutions, or highly staining substances. Such damage is of particular concern in heavy use situations such as in the hotel and catering industries, where there is very frequent heavy usage and repeated mechanised aggressive cleaning of ceramic tableware.
- [3] It is well known that physical and chemical resistance of surfaces may be enhanced by the use of appropriate surface coatings. For example the application and firing of a ceramic glaze applied to a piece of earthenware, stoneware, or porcelain gives much enhanced mechanical and surface characteristics relative to an unglazed piece of the same material.
- [4] One type of coating that has been suggested for use in surface protection for a wide range of hard surfaces is a silane-based coating. Such coatings are used in, for example the coating of glass surfaces for the automotive industry and are commercially available from a number of suppliers. A particularly preferred coating is available from Nanofilm Technology under the name Ultraseal AB5 .
- [5] The customary approach to using such coatings has been to apply a solution of the coating material to the surface to be protected using manual or automatic dispensing, spreading the material evenly over the surface by hand, desirably using an absorbent lint-free cloth, curing the applied solution, and wiping off excess material. This process can take 60 or more seconds for a single item of tableware, so is wholly uneconomic when applied to the mass manufacture or treatment of glazed tableware for hotel or catering use.
- [6] We have now found that it is possible to apply a surface treatment to the finished surface of glazed ceramic tableware on a mass production/treatment basis for the purpose of enhancing the tableware's performance in use, including improved resistance of the product to surface damage, and improved resistance of the surface to marking and staining. A further advantage given by applying such a surface treatment is that it results in an improved ease of cleaning.
- [7] According to the present invention there is provided a method of applying a silane-

based surface coating to ceramic tableware which consists of the following steps:

- [8] 1 Hydrating the surface of the ceramic tableware to be treated;
- [9] 2 Removing substantially all dust from the ceramic tableware to be treated;
- [10] 3 Applying a silane-based surface coating solution to the ceramic tableware to be treated;
- [11] 4 Allowing the silane-based surface coating solution to cure on the ceramic tableware to be treated; and
- [12] 5 Heating the ceramic tableware to be treated to a temperature sufficient to remove uncured silane-based surface coating solution from the ceramic tableware to be treated.
- [13] With regard to steps 1 and 2, these may occur in either order.
- [14] With regard to step 1, hydration may, in a preferred embodiment of the method of the present invention, be allowed to occur by leaving the ceramic tableware to be treated in atmospheric conditions for at least 24 hours, and preferably 24 hours, after it has exited the kiln. This allows atmospheric moisture to bond with the glaze surface of the ceramic tableware to be treated. In an alternative preferred embodiment of the method of the present invention, the ceramic tableware to be treated may be passed through a humidifying chamber or other like volume of high humidity air. This again allows moisture to bond with the glaze surface of the ceramic tableware to be treated. The purpose of the humidifying step is that when an item of glazed ceramic tableware leaves the kiln in which it has been fired, the glaze surface is extremely dry. Preferably the hydration will take place at ambient temperatures, most preferably substantially in the range of 18 -22 ° C.
- [15] With regard to step 2, any known dust removal means may be employed. A particularly preferred dust removal means is an air knife. This step is required because the presence of a surface layer of dust and/or particles of dust will prevent the silane-based surface coating solution from making uniform contact with the surface of the ceramic tableware to be treated.
- [16] With regard to step 3, the silane-based surface coating solution is most preferably applied to the ceramic tableware to be treated as a fine spray or mist. This application is most preferably from one or more separate nozzles so as to ensure a complete and even application of silane-based surface coating solution to the ceramic tableware to be treated. It is most preferred that the silane-based surface coating solution is deposited on the ceramic tableware to be treated at a rate of 0.02 to 0.04ml/dm² for a solution of Ultraseal AB5 This most preferably occurs in a spray booth or other enclosed area (hereafter simply referred to as a spray booth). The spray booth can be provided with a recirculation system for any coating solution that does not get deposited on the ceramic tableware to be treated if so desired. Furthermore, the spray booth may be provided with means to cause currents or turbulence in the atmosphere within the spray booth to

assist in securing even deposition of the coating solution on the whole surface of the ceramic tableware to be treated. The atmosphere within the spray booth is most preferably wholly or substantially dry (that is with no humidity). Most preferably, the atmosphere is substantially or wholly comprised of one or more inert gases. This is of assistance because the silane-based surface coating cures by reacting with water molecules. It is most preferred that the coating solution is stored in a pressurised container, said container being pressurised with an inert gas. Alternatively, the coating solution may be stored in other fashions as long as the coating solution is prevented from reacting with water molecules.

- [17] The silane based surface coating solution is formulated to include a silane molecule of the general formulation $R_nSi X_{(4-n)}$ where, 'R' denotes an organic group and can feature alkyl and aryl entities with or without bridging oxygens and reactive groups (C=C, C=O, COOH, epoxy, amine etc.), 'X' is typically one of two species: 1) A halide such as chloride ions or 2) An alkoxy group (OCH₃, OCH₂CH₃ etc); and 'n' denotes the number of 'R' or 'X' groups present, where 'n' can never exceed 4 and is a whole number dissolved or suspended in an organic solvent such that when the solution is cured, the cured material comprises in the range of 12 to 16 wt % silicon-oxygen entities and between 88 and 84 wt % organic material. Most preferably the silane based surface treatment solution is so formulated that when cured the cured material is composed of around 14 wt % silicon-oxygen entities and around 86 % organic material. Most preferably the silane molecule is SiCl₄.
- [18] When the silane based surface coating cures, the silane molecule undergoes hydrolysis when it reacts with water molecules to form a Si-OH group. In this process those water molecules are incorporated into/on the surface of the tableware being treated. The Si-OH groups then react with other Si-OH groups to form Si-O-Si bonds. This is termed condensation. These other Si-OH groups may either be found in separate molecules from the silane based surface coating or as part of the surface of the glaze to which the silane based surface coating is applied.
- [19] With regard to step 4, it is most preferred that the time allowed for the curing of the coating solution on the ceramic tableware (the cure time) is sufficient for the solution to cure as a result of reaction with the water bonded with the glaze of the ceramic ware. A preferred cure time has been found to be around 60 seconds. If an excessive cure time is allowed, any excess coating solution on the ceramic tableware may be difficult to remove subsequently.
- [20] With regard to step 5, the heating of the coated ceramic tableware that has been treated most preferably occurs in a kiln. The coated ceramic tableware is most preferably heated to a temperature in the range of 60 - 100 ° C. It is most preferred that the coated ceramic tableware is kept at a temperature in this range for around 2

minutes. This has the effect that any excess coating solution is removed by evaporation.

[21] Following treatment of the ceramic tableware to be treated according to steps 1 to 5, the ceramic tableware may be further treated if that is desired, for example to remove refractory pin marks from the reverse surfaces of the ceramic ware.

[22] In an alternative embodiment of the present invention, the ceramic tableware to be treated according to the present invention may be unglazed in which case its protective surface following treatment according to the present invention will only be the silane-based surface coating.

[23] The present invention will be further described and explained by way of example with reference to the accompanying drawings in which

[24] Figure 1 shows a schematic illustration of the manufacture of a batch of ceramic tableware according to an embodiment of the method of the present invention; and

[25] Figure 2 shows the results of some comparative testing

[26] With reference to Figure 1, a batch of ceramic tableware, for example plates, bowls, cups or the like, is manufactured out of a suitable ceramic material, for example, earthenware, stoneware or porcelain by a known process, glazed with a known glaze suitable for such a material and fired in a kiln 2. When the firing is complete the batch of ceramic tableware is removed from the kiln 2, loaded onto a processing trolley and moved to a hydration station 4. The hydration station is open to the air or normal atmosphere which in the UK has an average relative humidity in the range of 50 to 100%. Optionally, the hydration station may be surrounded with open containers of water, or other means of maintaining an average relative humidity of between 50 and 100%.

[27] The resting of the batch of ceramic tableware at the hydration station allows water molecules in the atmosphere to hydrate or interact with and bond to the surface of the glaze on the batch of ceramic tableware. It has been found that a rest period of 24 hours at ambient temperature and a relative humidity of between 50 and 100% is sufficient to result in a complete hydration of the surface of the glaze on the batch of ceramic ware. This approach to hydrating the surface of the glaze on the batch of ceramic tableware is particularly preferred because it requires the input of very low amounts of energy.

[28] The processing trolley is suitably adapted to carry a batch of ceramic tableware with a minimal contact between the trolley and the batch of ceramic tableware.

[29] It is possible to speed up the hydration of the surface of the glaze on the batch of ceramic tableware by ensuring that the average relative humidity of the atmosphere at the hydration station is close to 100%.

[30] Once the surface of the glaze on the batch of ceramic tableware has been hydrated it

is moved on the trolley through at least one sheet of laminar airflow generated by an air knife 6. The airflow blows off any dust that has settled on the batch of ceramic ware. The air knife or knives are so arranged that all of the surfaces of the batch of ceramic tableware are subject to impact of the sheet(s) of laminar airflow created by the or each air knife.

- [31] From the air knife(s) 6 the batch of ceramic tableware is moved to an enclosed spray booth 8. Spray booth 8 is most preferably capable of being made gas tight once the batch of ceramic tableware has been placed within it. Once the spray booth 8 has been made gas tight, the atmosphere within the spray booth is replaced with an inert gas such as nitrogen. A fine mist of Ultraseal AB5 or other silane based coating solution is introduced into the spray booth via a plurality of fine spray nozzles. The batch of ceramic tableware remains in the spray booth for sufficient time to allow between 0.02 to 0.04 ml/dm² of solution to settle on all the surfaces of the batch of ceramic tableware.
- [32] Once a suitable amount of solution has settled on all the surfaces of the batch of ceramic tableware, the batch of ceramic tableware is moved to a second kiln 10. The batch of ceramic tableware is moved at such a speed that between completion of its time in the spray booth 8 and it entering kiln 10 there is a period of about 60 seconds. Once inside kiln 10 the batch of ceramic tableware is heated to a temperature in the range of 60 to 100°C. The batch of ceramic tableware is kept at that temperature for around 2 minutes. The heating of the batch of ceramic tableware is has the effect of evaporating any excess solution off the ceramic ware.
- [33] Once processing of the batch of ceramic tableware in kiln 10 is complete the batch of ceramic tableware is moved to a cooling and packing station 12 where the batch of ceramic tableware is removed from the trolley and packed ready for transportation to a warehouse or a customer.
- [34] With reference to Figure 2, a test of the abrasion resistance of three samples of ceramic items, a first tile called STD in Figure 2, and first and second samples both of which had been treated according to the method of the present invention called IMPROVED 1 and IMPROVED 2 in Figure 2. In the test, each test piece was cut from the centre region of a plate; a 10cm x 10cm tile is used for the test. The initial gloss of the sample is measured using standard techniques. Each test piece is then abraded for 1000 revolutions using a mixture of de-ionised water and alumina pellets; a PEI tile abrasion rig is used to conduct the abrasion. After abrading, the gloss is re-measured; the final result is expressed as a percentage of the initial value. As may be seen, the IMPROVED 1 and IMPROVED 2 samples had a much higher resistance to abrasion than the STD sample.

Claims

- [1] 1. A method of applying a silane-based surface coating to ceramic tableware characterised in that it includes the following steps:
(i) Hydrating the surface of the ceramic tableware being treated;
(ii) Removing substantially all dust from the ceramic tableware being treated;
(iii) Applying a silane-based surface coating solution to the ceramic tableware being treated;
(iv) Allowing the silane-based surface coating solution to cure on the ceramic tableware being treated; and
(v) Heating the ceramic tableware being treated to a temperature sufficient to remove uncured silane-based surface coating solution from the ceramic tableware being treated.
- [2] 2. A method according to Claim 1 in which steps (i) and (ii) may occur in either order.
- [3] 3. A method according to claim 1 or 2 in which in the hydration of step (i) is caused by leaving the ceramic tableware being treated in atmospheric conditions for at least 24 hours.
- [4] 4. A method according to claim 1 or 2 in which the hydration of step (i) is caused by the ceramic tableware being treated being exposed to a highly humid atmosphere.
- [5] 5. A method according to any preceding claim in which step (ii) is achieved by use of one or more air knives.
- [6] 6. A method according to any preceding claim in which the silane-based surface coating solution of step (iii) is applied to the ceramic tableware being treated as a fine spray or mist.
- [7] 7. A method according to claim 6 in which the silane-based surface coating solution is deposited on the ceramic tableware being treated at a rate of 0.02 to 0.04ml/dm² for a solution of SiCl₄ in an organic solvent in a quantity such that when the surface coating solution is cured, silicon-oxygen entities are present at a range of between 14 and 16 wt % of the cured surface coating.
- [8] 8. A method according to any preceding claim in which step (iii) occurs in an atmosphere substantially or wholly comprised of one or more inert gases.
- [9] 9. A method according to any preceding claim in which the time allowed for the curing of the coating solution on the ceramic tableware in step (iv) is between 50 and 70 seconds.
- [10] 10. A method according to any preceding claim in which the time allowed for the curing of the coating solution on the ceramic tableware in step (iv) is 60 seconds.

11. A method according to any preceding claim in which temperature in step (v) is in the range of 60 - 100 ° C.
- [11] 12. A method according to claim 11 in which the coated ceramic tableware is kept in the temperature range of 60 - 100 ° C for around 2 minutes.
- [12] 13. An item of ceramic tableware to which a silane based surface coating has been applied according to the method of any of claims 1 to 12.
14. An item of ceramic tableware obtained or obtainable as a result of treatment of an item of glazed ceramic tableware by a method according to any of claims 1 to 12.
- [13] 15. A method of manufacture of an item of ceramic tableware comprising the steps of
- a) forming a body of material into an item of predetermined shape;
 - b) firing and glazing the shaped item;
 - c) treating the item according to the method of any of claims 1 to 12.

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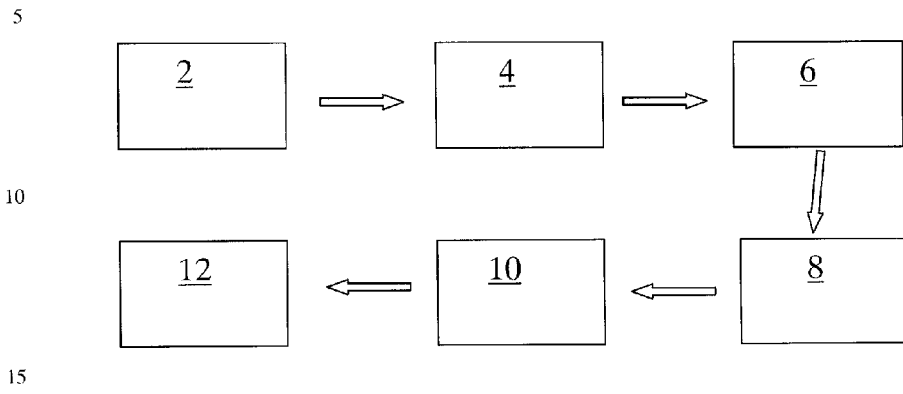
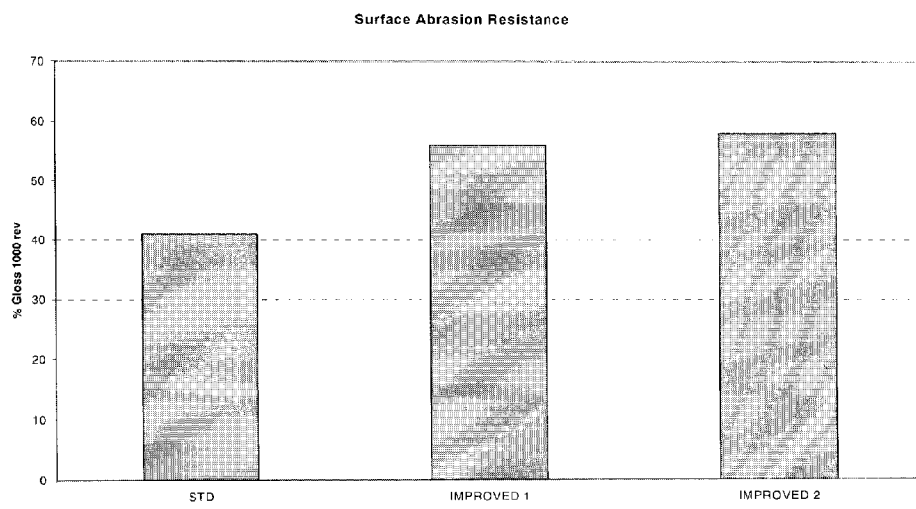


Figure 1



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Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/051064

A. CLASSIFICATION OF SUBJECT MATTER INV. C04B41/84 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C04B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 484 746 A2 (MATSUSHITA ELECTRIC IND CO LTD [JP]) 13 May 1992 (1992-05-13) examples	1-15
X	DE 101 49 933 A1 (SCHOTT GLAS [DE]) 30 April 2003 (2003-04-30) claims paragraphs [0001], [0011], [0012]	1-15
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Rosenberger, Jürgen

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0484746	A2	13-05-1992	CA 2054094 A1 26-04-1992
			DE 69122212 D1 24-10-1996
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DE 10149933	A1	30-04-2003	NONE