A METHOD OF IMPROVING WETTABILITY AND ENAMELLING The present invention relates to a method for improving the wettability of a metallic or non-metallic surface by a liquid such as enamel.

In order to easily clean surfaces, they are frequently covered by glazed tiles for example, the tile edges being spaced apart and the gaps therebetween being filled with grout. However, the grout tends not to be impervious to contaminants and consequently absorbs liquids which may be radioactive for example or may absorb harmful bacteria. Therefore, a method which makes the grout between tiles impervious and easily cleanable, by conventional wiping for example is highly desirable.

Out earlier patent specification number, EP 0 702 837, describes the replacement of conventional grout between tiles with a material mixture which is vitrifiable. The mixture is packed between tile edges and initially cured by drying and is then vitrified or glazed by the action of a laser. The melting and consequent vitrification of the mixture causes adjacent tiles to be welded together to form an impervious covering to a wall or tank for example. However, due to the large quantity of heat required to effect vitrification through the body of the grout and the necessarily high temperature differential between the molten grout and the adjacent tiles, cracking of the glazed surface of the tile adjacent the grout may occur under some circumstances. Clearly, cracking of the glazed tile surface is undesirable since this allows ingress of contaminant into the underlying porous body of the tile.

Enamelling is frequently used to form an easily cleanable surface coating over large areas. Pre-treatment of the substrate surface is necessary to ensure wetting of the surface and consequent bonding of the enamel to the substrate surface. Such surface pre-treatment may include cleaning with various chemicals, surface polishing or roughening and sometimes oxidation or deoxidation of the surface. If the surface pre-treatment is inadequate for any reason, imperfections may occur in the continuity of the enamel coating and which are difficult to repair.

An object of the present invention is to provide a method of improving the wettability of a metallic or non- metallic surface so as to facilitate the coating thereof with enamel.

A further object of the present invention is to provide an improved method of enamelling a substrate surface.

According to the present invention, there is provided a method of enamelling a substrate, the method including the steps of: treating a thin surface layer of said substrate with a laser beam so as to promote a change in the surface energy thereof; allowing the surface to cool; and, applying enamel thereto to wet and coat said substrate.

The heating of the substrate surface may or may not include melting thereof. The thickness of the surface layer which is affected is desirably thin, less than about 0.5mm for example. Because the heating rate is high due to the laser and the heat affected layer is thin, the rate of cooling of the heated layer is very high, <BR> <BR> <BR> <BR> typically 103-106 °C/sec. Since the cooling rate is high even under normal atmospheric conditions, special microstructures may be produced at the substrate surface such as very fine grain sizes in metals and ceramics which have been melted or amorphous structures in some cases or solid state phase transformation, e. g. heating steel from a ferritic structure to an austenitic structure which may transform to a martensitic structure on cooling.

Such surface modifications can lead to beneficial changes in substrate surface energy which can improve wetting characteristics which determines the bonding between the substrate and enamel coating.

When a drop of liquid is placed on a solid surface it may remain as a substantially spherical drop or it may spread out and wet the surface. The angle at which the liquid meets the surface at the interface is known as the contact angle. In practice, for wetting to occur the contact angle must be less than 90°. If the contact angle is greater than 90° wetting of the surface does not occur and consequently no bonding or adhesion of an enamel for example to the surface occurs. When a drop of liquid is in free space it is drawn into a substantially spherical shape due to surface tension forces. When such a drop of liquid is brought into contact with a solid surface, the final shape taken by the drop, and thus whether it will wet the surface or not, depends upon the relative magnitudes of the molecular forces that exist within the liquid (cohesive forces) and between the liquid and the solid (adhesive forces); the index of these effects being <BR> <BR> <BR> <BR> the contact angle 0 which the liquid subtends with the<BR> <BR> <BR> <BR> <BR> solid. A is related to the solid (ysv) and liquid(y) surface energies and the solid/liquid interfacial energy <BR> <BR> <BR> <BR> (Ysl) through the principle of virtual work expressed by Young's equation: Ysv = Yiv CosO+y,i If an equilibrium is established, the relation of 0 to rsv, rlv and rsl is described by the rearranged Young equation: <BR> <BR> <BR> <BR> <BR> <BR> coso<BR> <BR> <BR> <BR> <BR> rlv Consequently, if the right hand side of this equation exceeds zero, the liquid will wet the solid surface.

Thus, when 0 is less than 90° wetting will occur and when <BR> <BR> <BR> <BR> 9 is greater than 90° non-wetting will result. Clearly,<BR> <BR> <BR> <BR> <BR> <BR> to achieve wetting Ysv must be greater than y,,,.

The effect of the method of the present invention is to modify the surface energy of the solid substrate surface (ysv) so as to promote wetting thereof by the enamel.

The substrate surface is heated to a high temperature, typically above 500°C which will normally decompose any organic surface contaminants and help clean the surface.

Laser power density is preferably above 500W/cm2 for non- metallic materials such as ceramics for example. For metals the minimum power density is preferably substantially higher.

The laser may generate a thermal or photo-chemical effect on the substrate surface. In the case of thermal effect to heat or melt the surface layer of the substrate, lasers such as CO2, Nd-YAG, semi-conductor or a fibre laser generating an infra-red beam may be used for example or a copper vapour laser operating in the visible spectrum may be used. Where a photo-chemical effect is required an excimer laser operating at a UV wavelength may be used.

Laser beam scanning speed will be dependent upon the laser power density and the thermal properties of the substrate being treated, the higher the power density the faster the scanning speed. As an example, a typical scanning speed when treating an alumina based substrate surface with a diode laser of 45W and having a lmm beam spot size will lie in the range of 5 to 20mm/sec.

The treated surface may be enamelled by the application of molten enamel thereto such as by plasma spraying for example or dipping in a bath of molten enamel.

Alternatively, the enamel may be applied in a particulate form in a carrier/binder and melted by the application of heat, e. g. by a laser beam for example. It should be remembered that the enamelling process only involves the melting of the enamel per se and does not involve the melting of the substrate on which the enamel is being coated. Thus, the heat input is considerably less than when fusion of grout and tile edges and welding together of glazed tiles such as described in EP 0 702 837 occurs.

Consequently, cracking of the tile surface glazing does not occur as the heating differential is greatly reduced.

During laser treatment of the substrate surface, inert gases may be used to provide a protective shroud to the laser beam/surface interaction zone. Alternatively, gases may be used to generate a reaction between the gas and treated surface, e. g. in the case of the use of oxygen to oxidise the surface for example during laser irradiation. Therefore, an advantage of the present invention is that surface preparation in a single step may be achieved in-situ.

A further advantage of the present invention is that the use of cleaning chemicals may be greatly reduced or eliminated and thus also obviate the need for safe disposal of such chemicals. Additionally, materials which are sensitive to chemical attack may be surface treated with a laser according to the present invention.

A yet further advantage of the present invention is that repair of damaged enamel coatings, in-situ, or for the sealing of surfaces using enamel outside of a factory environment.

In order that the present invention may be more fully understood, an example will now be given by way of illustration only with reference to the accompanying drawings, of which: Figure 1 shows a schematic side view of a substrate surface being laser treated; Figure 2 shows a schematic side view of the substrate surface of Figure 1 being coated with enamel; and Figure 3 which shows a cross section through a tiled surface having a grout region sealed with enamel according to the present invention.

Referring now to the drawings and where the same features are denoted by common reference numerals.

Figure 1 shows a substrate 10 having a laser beam 12 scanned across the surface 14 in the direction 16 so as to treat by heating or melting a thin surface layer 18.

The treated layer 18 is protected during treatment by a shroud gas indicated by the arrow 20 from a jet 22. The surface layer 18 is very thin and owing to the large heat sink constituted by the substrate 10 rapidly cools to ambient temperature. Figure 2 shows the treated substrate 10 and layer 18 of Figure 1 to which a particulate layer 30 of an enamel composition has been applied. A laser beam 32 (which may or may not be the same laser beam as 12 of Figure 1) is scanned across the surface in the direction 34 to melt the enamel powder 30 to form a solid, impervious coating 36 on the substrate 10. A protective shroud gas 38 is also provided.

Figure 3 shows a cross section through two glazed tiles 50 having a gap partially filled with grout 52 therebetween and an overlying enamel layer 54. The tiles are fixed by a known method to a substrate 56 such as a wall. Ceramic tiles are frequently used to provide easily cleanable surfaces where hygienic environments are required such as in hospitals, food processing areas and bio-research laboratories for example. However, as noted above, the grout between tiles is usually the vulnerable area where contamination can accumulate and is not easily cleanable to the standards needed. Although epoxy resins have been used for grouting in more recent times, their corrosion resistance is lacking in some environments and also has poor wear resistance. Consequently, it would be desirable to be able to seal the grout with a similar material to the tile glaze. It is not possible to seal conventional grouting materials by vitrification as vaporisation and decomposition occurs. Furthermore, as noted above with regard to EP 0 702 837, where the whole body of a vitrifiable grout material is so vitrified, cracking of the tile glaze can occur which is also counterproductive. In this example, a compound of mixed vitrifiable oxide powders selected from the group including for example, silica, alumina, iron oxide (s), magnesium oxide, zirconia, zinc oxide and chammotte is prepared. The oxide powders are sieved to ensure a particle size of less than about lootm and thoroughly mixed together with approximately 50 wt% water diluted sodium silicate solution so as to form a manageable paste. The paste is then filled into the gaps between the tiles 50 to a level below the surface and allowed to cure for about 12 hours. Carbon dioxide gas in the atmosphere assists in curing the grout composition or carbon dioxide gas may be blown on the grout to accelerate curing. The surface of the cured grout 52 is then irradiated by a diode laser so as to generate a thin surface layer 60 of melted and solidifie ceramic material of crystalline structure to form a base for the subsequent enamel layer 54 as described with reference to Figures 1 and 2. The surface layer 60 is overlaid with a thin layer (about 250pm) of enamel frit powder in a carrier of about 20 wt% of white spirit to form a manageable paste. The enamel frit composition may comprises mainly SiO2, B203, Na20, Mn, F203 and small quantities of Ba203, Al203 and nickel oxide, the particle size being less than about 75pm. The enamel frit paste is allowed to cure for one to two hours and then irradiated immediately with a defocused diode laser beam so as to melt the frit and cause it to wet the underlying treated grout. Neither the tiles nor the underlying grout is melted, only the frit. Naturally, the method of the present invention requires that the enamel has a lower melting temperature than either the tiles or the grout compound.

In the example given above, the diode laser operates between 10-120W with a radiation wavelength of 810nm 20nm. The laser beam is delivered through a 600jj. core diameter optical fibre, the end of which is connected to a 2: 1 focusing lens. The defocused beam to melt the grout and the enamel frit has a beam spot diameter of 2-3mm.

The laser beam scanning speed is between 2-30 mm/s. 3 1/min of coaxially blown oxygen assist gas is used to shield the laser optics and to assist the process.

In the example given above, it was found that the laser treated grout surface enabled wetting thereof by the molten enamel and facilitated complete covering. Comparative tests on the untreated grout surface revealed no bonding of the enamel to the grout surface.