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PROCESS FOR MAKING A PATTERN ON AN ARTICLE BY LASER MARKING AND ELECTRO-COATING

Field of the invention

- 5 This invention relates to a process for creating a pattern on an article by laser marking and electro-coating and refers particularly, though not exclusively, to the process for making a multi-colour pattern on a decorative article by laser marking and electro-coating.

Background to the invention

- 10 At present, when making a multi-colour pattern on the decorative article such as, for example, a watchcase frame or bezel, it is achieved by firstly pressing the article (normally of metal) to achieve the pattern, and then manually inking the patterned area. With pressing, it is very difficult to achieve a fine pattern.
- 15 US patent for 4,432,855 of Romankiw discloses the cleaning of an article using an alkaline cleaner; rinsing, etching, then rinsing again; further etching then electroplating with nickel; and then rinsing but not drying. The article is then either completely covered with a dielectric mask with a laser being used to remove the dielectric mask in the
- 20 desired pattern to provide a patterned mask, spraying with water, electroplating through the patterned mask, using a dissolving solvent to remove the mask, then rinsing, or, alternatively, using laser beams to define the desired pattern on the article, and then electroplating using laser enhancement.

Japanese application 3-277782 uses an etching method to pattern an uneven surface on a watchcase. The photoresist process and electro-coating are used to create a mask. Ultraviolet light is used to generate a pattern, followed by chemical etching.

5 European patent application 0 459 461 A1 discloses the use of a process where the surface of the article is first coated with a first layer of a suitable metal by amongst others, electroplating. The metals given by way of example are copper, silver, gold, platinum, iridium, osmium, palladium, rhodium, ruthenium, and an alloy of them. A laser
10 is then used to create a desired pattern on the article surface by removing the first layer. Electroplating is then used to plate the patterned area with a second metal or a different colour to the first, thereby giving an article with enhanced decorative appearance.

In the above prior art, only electroplating or chemical etching are
15 used to make a fine pattern on a decorative article. Electroplating has few colour choices, and etching only provides the metal itself as the colour.

Japanese 60-184696 discloses a colouring method using electro-coating of organic material onto an insulative board. In this process, an
20 intermediate conductive film must be printed over the insulative board as a pattern, with electro-coating being used over those areas covered by the conductive film. Although many colours of electro-coating and the formulas are disclosed in the specification, it does not mention how to make a pattern into the metal of the article.

25 The present invention therefore has as its principal object the making of a pattern on an article by laser marking and electro-coating.

Brief description of the invention

With the above and other objects in mind the present invention provides a process for making a pattern on at least one surface of an article including the steps of:

- 5 (a) providing a protective film over the article;
- (b) creating a predetermined pattern in the protective film by
 using a controlled laser marking system to remove the
 protective film where the pattern is to be created;
- 10 (c) etching the article to obtain a fresh surface by removing
 any inert layer created on the surface as a result of the
 use of the laser;
- (d) electro-coating the article to provide a desired coating of
 desired colour in the pattern on the surface of the article;
- 15 (e) precuring the article by the application of heat at a first
 temperature for a first period of time;
- (f) removing the protective film to reveal the article with the
 desired pattern on the surface; and
- (g) subjecting the article to final curing by the application of
 heat at a second temperature for a second period of time.

20 The article will normally be of a metal or a pre-plated metal, with the plating being of a material such as, for example, gold, silver or platinum. However, the invention is not so limited.

- Preferably, the full cover protective film is applied to the entire article. More preferably, it is applied by immersion. Alternatively, it may be applied by spraying. More preferably, the full cover protective film is dried in an oven at a third temperature for a third period of time.
- 5 For example, the third temperature may be 120°C and the prescribed time may be 20-30 minutes.

- Advantageously, the material of the full cover protective film is grey or black in colour so as to absorb the energy of the laser. More advantageously, the laser marking system is under computer control.
- 10 The laser beam may burn the protective film as well as the surface of the article to achieve the desired pattern along a pre-programmed route. The pattern may be to a depth which may be determined by the output energy, laser pulse rate and laser beam moving velocity.

- The first temperature may be, for example, 140-150°C, and the
- 15 first period of time may be, for example, 30 minutes.

- It is preferred that the removal of the full cover protective film is by immersion in a sodium hydroxide solution. This is preferably a 10% sodium hydroxide solution. It may be at room temperature or it may be heated to a fourth temperature. The time for immersion may be any
- 20 suitable period of time such as, for example, 5 minutes. Water jet spraying may be used after immersion to ensure all masking film is removed.

The second temperature may be, for example, 180°C, and the second period of time may be, for example, 30 minutes.

- 25 The protective film may contain a carboxyl group. It may also contain pigments such as, for example, carbon black; as well as

solvents such as, for example, butyl alcohol and ethyl ether; and an inorganic filler.

Description of drawing

In order that the invention can be fully understood there shall
5 now be described by way of non-limitative example only a preferred embodiment of the present invention, the description being with reference to the attached drawings in which:

Figure 1 is a flow chart which provides an exemplary form of the process of the present invention; and

10 Figure 2 is a vertical cross-sectional view (on a significantly enlarged scale) of part of an article after the process of the present invention has been used.

Description of preferred embodiment

With reference to the drawing, the process of the present
15 invention firstly provides a process for providing a pattern on an article by laser marking and electro-coating. The article 11 has a surface 14 which may be smooth, even, or not smooth and uneven. Therefore, it can be applied to articles 11 of varying natures, and quality.

The first step 1 in this process is to provide a full cover
20 protective film 10 over the surface 14 of the article 11. This may be achieved by either immersion or spraying, depending on the size and shape of the article 11. At step 2, the full cover protective film 10 is dried in an oven for a period of, for example, 20-30 minutes at a temperature of, for example, 120°C.

The material of the protective film 10 must have all normal properties of a masking film such as ease of handling, operating, and chemical resistivity. Furthermore, it is preferred that it is either grey or black in colour so as to easily absorb the energy of the laser. It should
5 also be able to be easily removed in mild conditions which would not damage the electro-coated layer 13 in the process. It is preferred that the full cover protective film 10 have an acidic polymer as its main component and, by adding active carbon, filler and solvent, the final material for the full cover protective film 10 can be created. The film 10
10 should be able to withstand any acidic operating conditions and be easily able to be removed in an alkaline solution.

One example of a suitable full cover protective film 10 is an alkaline soluble plating protective film. Such a film has good resistance to most plating chemicals, and is easily soluble in a relatively strong
15 alkaline environment. It is preferably able to resist the acid used in the etching process. It has a high acid value derived from its main resin, which has a carboxyl group. Under acidic etching or plating, it will remain intact as the carboxyl group is an H⁺ donor. However, in the stripping process a strong alkaline solution is used.

20 The film 10 may comprise maleic resin in the range 20 to 40% by weight; pigment(s) such as, for example, carbon black in the range 2 to 4% by weight; an inorganic filler in the range 15 to 25% by weight; and solvents in the range 33 to 65% by weight. Suitable solvents include butyl carbitol in the range 3 to 5% by weight, and ethyl ether in
25 the range 30 to 60% by weight.

Step 3 is when the predetermined pattern 12 is produced in the film 10 by using an Nd YAG laser marking system under computer

control. The laser beam will burn the full cover protective film 10 off the surface 14 in the predetermined pattern 12 and may also provide the pattern 12 in the surface 14 of the article 11 at the required depth. This is achieved by the laser beam following the pre-programmed route.

- 5 The depth of the pattern 12 is determined by the output power (current), laser pulse rate, and laser beam moving velocity. By adjusting those three aspects, and other operating conditions as desired, a fine pattern 12 up to 10 micron resolution may be able to be achieved.

- 10 The next stage 4 in the process is etching to obtain a fresh surface by removing the inert layer created as a result of the laser. This provides a fresh, clean surface of the material of the article 11. For most base metals such as, for example, stainless steel, copper, titanium, brass, and so forth, an etching solution based on ferric chloride may be used. This may be 20 to 30% by weight of ferric chloride; 5 to 10% by weight of hydrogen chloride; and the remainder water. For a material such as stainless steel, its etching speed is 10 to 15 um/minute at room temperature. For other materials or pre-plated materials, the etching solution is chosen to match the properties of the material.

- 25 The electro-coating step 5 follows. Electro-coating is a method of organic finishing which uses electrical current to deposit the paint or other coating material 13 on the conductive surface 14. There are many types of commercial electro-coating processes such as, for example, a cathodic poly-urethane E-coating material. One example of this is sold under the trade mark "CLEARCLAD". This is an excellent choice because of its variable colours, and it has significant resistance to chemicals and ultraviolet light. Electro-coating may be under a

desired voltage range such as, for example, 10-15 volts. This may be for a prescribed period such as, for example, 60 seconds. This may achieve a result of a layer 13 of 6-10 micro thickness in the desired color.

- 5 Pre-curing step 6 then follows for a time such as, for example, 30 minutes at a temperature of, for example, 140-150°C. This enhances the alkaline resistance of the electro-coating layer 13.

- By carefully selecting the film 10 and the pre-curing process 6, the removal of the remainder of the film 10 at step 7 may be relatively
10 easily achieved. A sodium hydroxide solution may be used such as, for example, a 10% sodium hydroxide solution. This may be at a suitable temperature such as, for example, room temperature. By immersing the article 11 in the solution for a prescribed time such as, for 5 minutes, the film 10 is loosened and will drop into the solution.
15 Water jet spraying may be used to ensure all film 10 is removed. The pattern with the desired colour then appears.

- Final curing in step 8 can provide an electro-coated layer 13 of excellent chemical, ultraviolet light and wear resistance. It may be of any suitable thickness such as, for example, 5 to 8µm. The curing may
20 be at a suitable temperature such as, for example, 180°C for a preferred time such as, for example, 30 minutes.

- It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or
25 drawings. All of these different combinations constitute various alternative aspects of the invention.

It will also be understood that the term "comprises" (or its grammatical variants) as used in this specification is equivalent to the term "includes" and should not be taken as excluding the presence of other elements or features.



The claims:

- 1 A process for making a pattern on at least one surface of an article including the steps of:
- (a) providing a protective film over the article;
 - 5 (b) creating a predetermined pattern in the protective film by using a controlled laser marking system to remove the protective film where the pattern is to be created;
 - 10 (c) etching the article to obtain a fresh surface by removing any inert layer created on the surface as a result of the use of the laser;
 - (d) electro-coating the article to provide a desired coating of desired colour in the pattern on the surface of the article;
 - 15 (e) precuring the article by the application of heat at a first temperature for a first period of time;
 - (f) removing the protective film to reveal the article with the desired pattern on the surface; and
 - 20 (g) subjecting the article to final curing by the application of heat at a second temperature for a second period of time.



- 2 The process of claim 1, wherein the full cover protective film is applied to the entire article by immersion.
- 3 The process of claim 1, wherein the full cover protective film is applied to the entire article by spraying.
- 5 4 The process of any one of claims 1 to 3, wherein the full cover protective film is dried in an oven at a third temperature for a third period of time.
- 5 The process as claimed in claim 4, wherein the third temperature is 120°C and the third time is in the range of from
10 20 to 30 minutes.
- 6 The process of any one of claims 1 to 5, wherein, the material of the full cover protective film is grey or black in colour so as to absorb the energy of the laser.
- 7 The process of any one of claims 1 to 6, wherein the laser marking system is under computer control and burns the protective film to achieve the desired pattern along a pre-programmed route.
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- 8 The process of claim 7, wherein the pattern depth is determined by the output energy, laser pulse rate and laser beam moving
20 velocity.
- 9 The process of any one of claims 1 to 8, wherein the pattern is also created in the surface of the article by the laser.



- 10 The process of claim 9, wherein the first temperature is in the range of from 140-150°C, and the first period of time is 30 minutes.
- 5 11 The process of any one of claims 1 to 10, wherein the removal of the full cover protective film is by immersion in a sodium hydroxide solution.
- 12 The process of claim 11, wherein the sodium hydroxide solution is a 10% sodium hydroxide solution.
- 10 13 The process of claim 11 or claim 12, wherein water jet spraying is used after immersion to ensure all of the full cover protective film is removed.
- 14 The process of any of claims 1 to 13, wherein the second temperature is 180°C, and the second period of time is 30 minutes.
- 15 15 The process of any one of claims 1 to 14, wherein the protective film comprises maleic resin in the range 20 to 40% by weight; pigments in the range 2 to 4% by weight; inorganic filler in the range 15 to 25% by weight; butyl carbitol in the range 3 to 5% by weight; and ethyl ether in the range 30 to 60% by weight.