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(54) Title of invention

**Timepiece dial**

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(73) Proprietors
**Kabushiki Kaisha Suwa Seikosha**
**(Japan)**
**4-1 2-chome Nishi-shinjuku**
**Shinjuku-ku**
**Tokyo**
**Japan**

(72) Inventors
**Masami Kasai**
**Masao Kanai**
**Akira Okubo**

(74) Agent and/or Address for Service
**J. Miller & Co.,**
**Lincoln House,**
**296-302 High Holborn,**
**London WC1V 7JH**

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(56) Documents cited
**GB 1175832**

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Fig. 1(1).


Fig. 2(1).


Fig. 1(2).

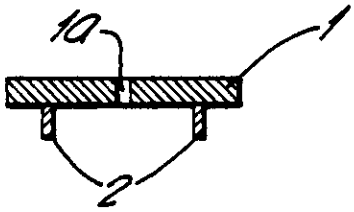



Fig. 2(2).


Fig. 1(3).

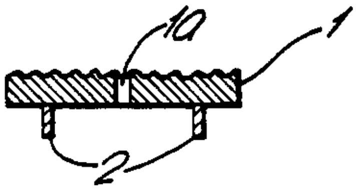



Fig. 2(3).

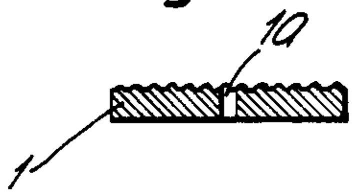



Fig. 1(4).

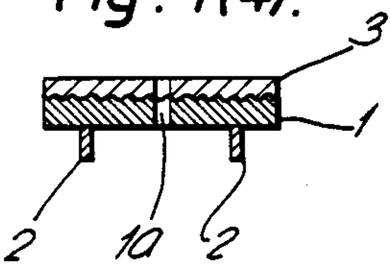



Fig. 2(4).

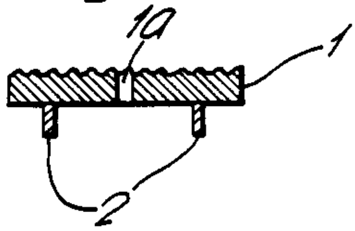



Fig. 2(5).

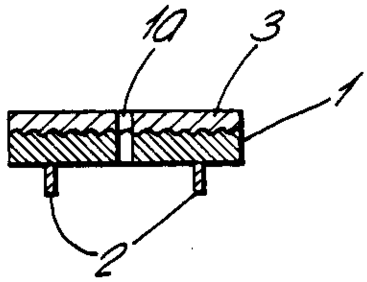


Fig. 3.

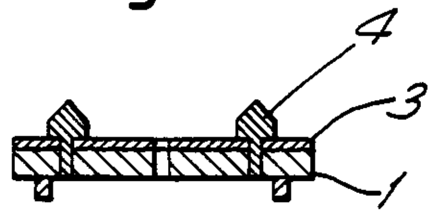



Fig. 9(1)

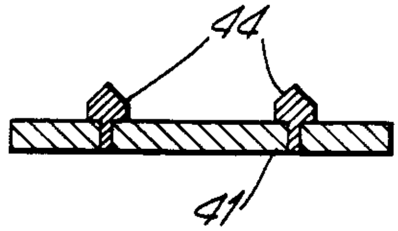
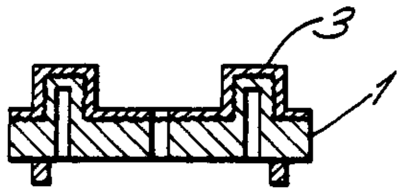



Fig. 4(1)

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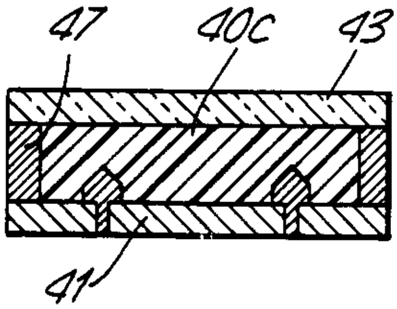


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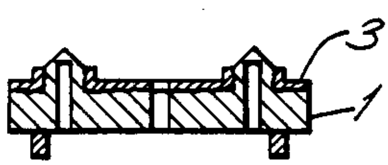



Fig. 9(3).

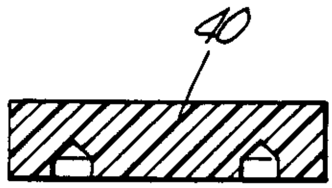



Fig. 8.

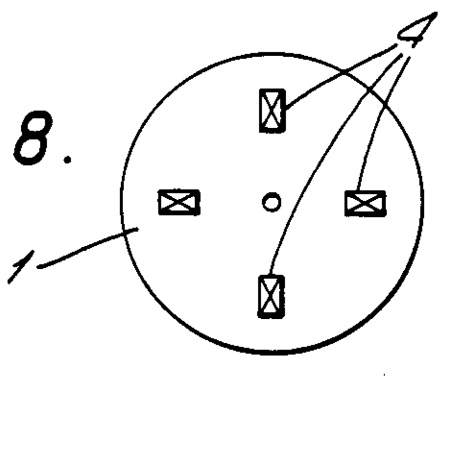
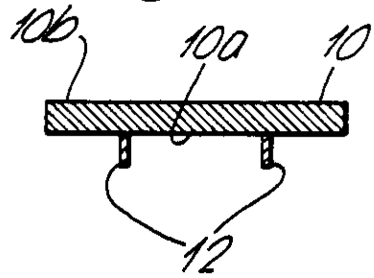


Fig. 5(1).


Fig. 5(2).

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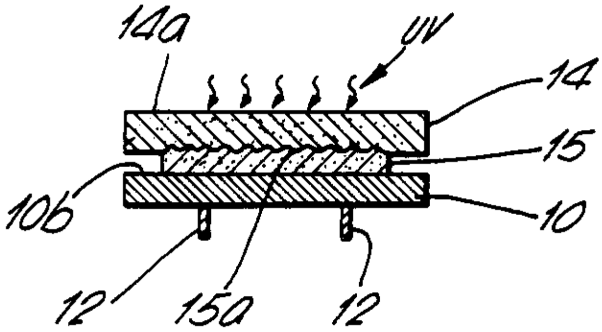



Fig. 5(4).

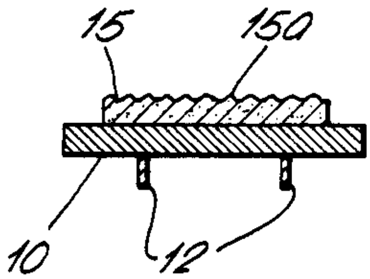
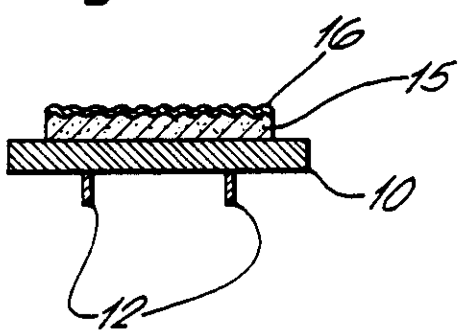



Fig. 5(5).

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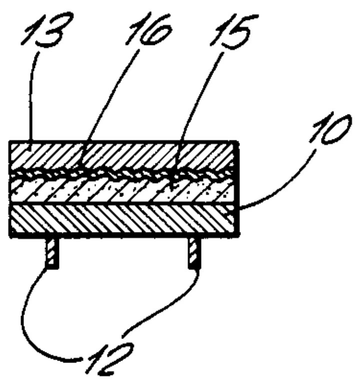

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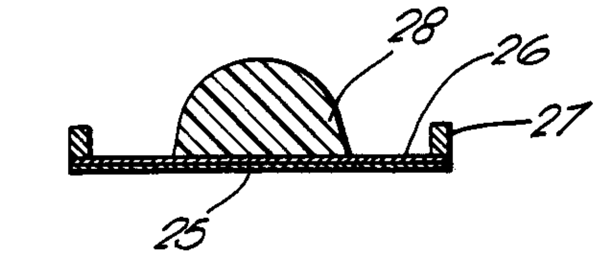



Fig. 6(2).

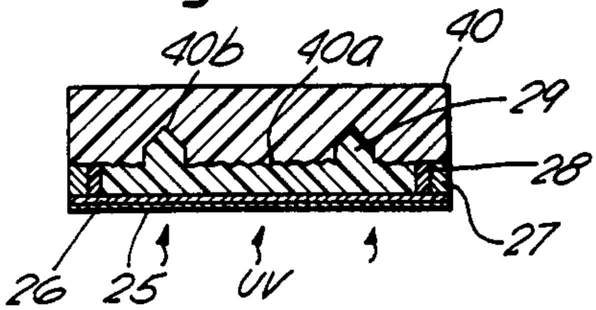



Fig. 6(3).


Fig. 6(4).


Fig. 6(5).

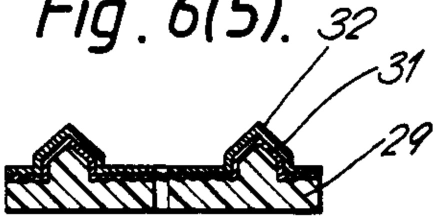



Fig. 7(1).

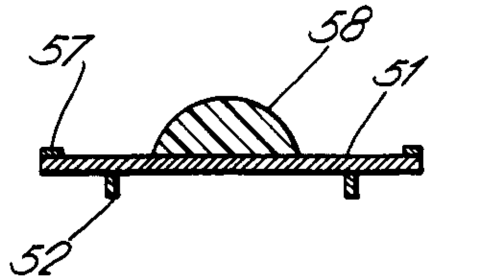



Fig. 7(2).

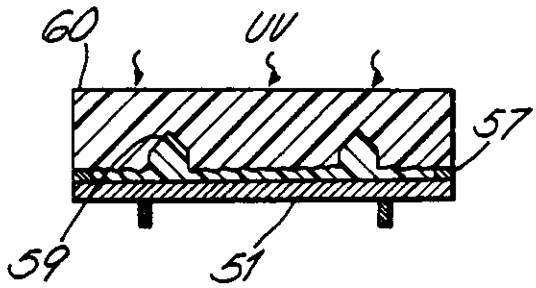



Fig. 7(3).

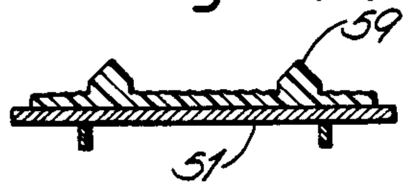



Fig. 7(4).

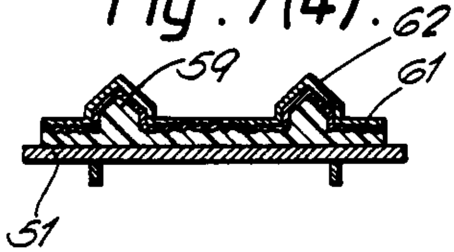
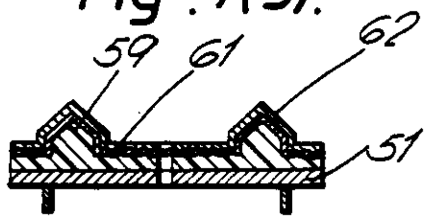



Fig. 7(5).



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"TIMEPIECE DIAL"

This invention relates to a timepiece dial and to a method of making same, and, although not so restricted, it relates more particularly to a watch dial provided with a surface design, or one or more letters, symbols, pictures, marks and the like whose concave and convex portions are formed in a photosensitive resin layer.

In conventional processes for manufacturing watch or other timepiece dials, it is difficult or impossible to reduce manpower by automation or mechanization. Dials, however, are often produced in small quantities so that the conventional processes are very costly.

According to the present invention, there is provided a timepiece dial comprising a photosensitive layer having a surface at least part of which is uneven by reason of having one or more convex or concave portions and which has been photopolymerised, and a metal layer which covers at least the said uneven part.

Preferably the whole of the photosensitive layer has been photopolymerised. Preferably also the whole of the said surface is covered by the said metal layer.

The said uneven part may be formed with at least one indicium or aperture and/or with a design.

The photosensitive layer is preferably provided on a metal base plate and an adhesive agent may be provided between the metal base plate and the photosensitive layer.

The dial preferably comprises a transparent coating layer which covers at least the said part of the said surface.

Preferably the surface of the transparent coating layer remote from the said surface of the photosensitive layer is printed.

The adhesive agent may be a mixture of a hydrolytic silicon compound having an ethylene unsaturated substituent group, hydrolytic tetraalcoxy silane and a catalytic component. Thus the catalytic component may be tetraalcoxy titanium or an aqueous acid.

Preferably the thickness of the photosensitive layer is 8/100mm or more.

The metal layer may comprise an Ni group electroless plating layer, an electrolytic subplating layer and a final plating layer.

Preferably, the thickness of the Ni group electroless plating layer and of the electrolytic subplating layer is in the range 1,500Å to 3,500Å. The said electrolytic subplating layer may be constituted by a plating of a single metal, or may be constituted by an alloy plating of Ni, Co or Fe.

If desired, the colour of said uneven part and the colour of the metal layer are different from each other.

The transparent coating may be constituted by a layer not thicker than 800Å which is superimposed on said metal layer. Preferably, the said transparent coating layer is a film containing at least one hydrolytic silicon compound.

If desired, the photosensitive layer has a part other than the said uneven part which is provided with a colour coating or with mat coating.

The invention also comprises a method of making a timepiece dial comprising providing a photosensitive layer with a surface at least part of which is uneven by reason of having one or more convex or concave portions, photopolymerising at least the said uneven part, and covering at least the said uneven part with a metal layer.

Preferably, the polymerisation is effected by ultraviolet light.

The ultraviolet light may be directed onto the said layer by way of a transparent or semi-transparent mould which has been used to form the said surface.

The invention is illustrated, merely by way of example, in the accompanying drawings, in which:-

Figures 1(1) to 1(4) are sectional views illustrating a conventional manufacturing process for producing a butler finished watch dial,

Figures 2(1) and 2(4) are sectional views illustrating a conventional manufacturing process for forming a watch dial by a face-stamping process,

Figure 3 is a sectional view of a known watch dial in which letters or other additional parts are implanted,

Figures 4(1) and 4(2) illustrate a known method of making a watch dial by coining,

Figures 5(1) to 5(6) are sectional views illustrating a first embodiment of a method in accordance with the present invention for producing a dial of a wrist watch or other timepiece,

Figures 6(1) to 6(5) illustrate a second embodiment of a manufacturing method in accordance with this invention,

Figures 7(1) to 7(5) illustrate a third embodiment of a manufacturing method in accordance with this invention,

Figure 8 is a plan view of a watch dial in accordance with this invention, and

Figures 9(1) to 9(3) illustrate a process for making a plastics mould or die.

There are at present two known methods for forming the base plate of a watch dial. In one of these methods a "butler-finished" dial has a hairline design, a radial design or the like provided on the surface of the base plate of the dial, and in the other of these methods a stamped dial is formed by a stamping process.

In the said one method, i.e. the butler-finished method, the external shape of a base plate 1, which may be 0.3mm thick, and a central hole 1a therein are press-cut from a nickel-copper alloy or other board, as shown in Figure 1(1).

Feet 2 are then fixed to the base plate 1 as shown in Figure 1(2).

There are at present two methods for fixing the feet 2 to the base plate 1. In one of these methods for fixing the feet, silver wax is utilized. The feet 2 are formed of silver wax which has been introduced into a copper pipe. The copper pipe portions of the feet 2 are temporarily fixed to the base plate 1 by resistance welding, and the base plate 1 is then kept in a furnace at a temperature of 800°C for 5 minutes so as to melt the silver wax in the copper pipe portions. This results in completely fixing the feet 2 to the base plate 1. As a result of this method, the base plate does not have any projecting portion or other deformation of the surface of the base plate 1 to which the feet 2 are fixed. However, the silver wax is melted at a high temperature (800°C), so that the material of the base plate 1 is annealed. For example, if the base plate 1 consists of BS(brass), the Vickers hardness which was 180Hv before it was put in the furnace decreases to 80Hv, which limits the thickness of the base plate. A base plate of less than 30/100 mm thickness cannot be used in practice. Further, the equipment required for heating the base plate at a high temperature of 800°C is large.

In the second of the said methods for fixing the feet, sharp-pointed feet 2 composed of pure copper are fixed into the base plate 1 by pressing the feet into the latter and resistance welding by passing an electric current between the base plate 1 and the feet 2. The sharp-pointed portions of the feet 2 are fixed by locally heating, since they have a high resistance. In this method, heat is generated only at the sharp-pointed portions. Thus, the hardness of the base plate 1 is maintained due to the fact that the heating is merely local. However, the pressure which is applied so as to firmly fix the feet 2 to the base plate 1 gives rise to projections or other deformations of those portions of the base plate 1 which carry the feet 2. That is, projections of 10 to 20 μm occur on the side of the base plate 1 opposite to the feet 2, which affects its appearance, and these projections have to be removed to produce an even surface. After fixing the feet 2 in position, moreover, the surface of the base plate is polished with a feather cloth to provide it with a specular surface. This polishing process with a feather cloth, however, requires high skill. If even a small blemish remains after such polishing, the appearance is badly affected in butler finishing. Further, when the material of the base plate has any defects (such as impurities and the like), a specular surface cannot be obtained. Thus, a special material having little impurity is required.

The butler design, as shown in Figure 1(3), is formed by using a special processing machine tool (not shown). There are ten kinds of butler designs, e.g. a radial design, a hairline design and the like, for which special processing machine tools are required.

After that, a honing process is carried out by means of a special processing machine (not shown). This honing process is important for determining the texture of the dial, and a number of different kinds of honing processes have been used. Surfaces having different textures can, for example, be formed by various kinds of abrasive grain, and by varying grain diameter and honing time.

Then plating is carried out, e.g. Ni plating for a first plating, followed by Ag plating, Au plating and the like for a final plating. Thus, as shown in Figure 1(4), the dial is provided with a coating layer 3.

Subsequently lacquer blasting and printing are carried out so that a print-type dial is completed.

In the case of the stamping method for producing a dial, a base plate 1 is press-cut so as to stamp out the raw material into the form shown in Figure 2(1).

An annealing treatment is then carried out, such treatment being required to facilitate a subsequent face-stamping process.

After that, as shown in Figure 2(2), a design is formed on the base plate 1 by a face-stamping process. The face-stamping process comprises forming a design on the surface of a metal mould and pressing the latter (at a pressure of 100 tonnes) against the base plate 1 to effect cold working so as to give a desired pattern to the base plate 1. Since this face-stamping process is carried out by friction pressing at a pressure of 100 tonnes, very large and heavy equipment is required for processing a small dial. Next, as shown in Figure 2(3), a central hole 1a and the external shape of the base plate 1 are formed by press cutting.

Feet 2 are then fixed to the base plate 1 with silver wax as shown in Figure 2(4), with the result that fixing the feet by resistance welding cannot be used. This is because the surface of the base plate 1 has been already provided with the required design, so that the projecting portions of the surface of the base plate, which would arise from fixing the feet by resistance welding, cannot be removed.

Subsequently, a plating treatment, a coating to produce a coating layer 3 as shown in Figure 2(5) and a printing are carried out so as to produce a printed dial.

As described above, a friction pressing of 100 tonnes is required for forming a stamped dial, while ten different work machines corresponding to the various designs are required for forming dials provided with butler design patterns. Further, both of the above-mentioned processes require high skill.

Furthermore, there are two methods for fixing the feet,that is, by resistance welding and by using silver wax, which cannot be combined under the present conditions.

As indicated above, it is technically difficult to automate and provide an assembly line for a method involving a number of differentmanufacturing processes. Even if it were possible, a large amount of development cost and plant investment would be required.

In Figure 3 there is shown a further known printed dial 1 which may be made by the processes described above, additional parts 4 such as letters, marks or parts provided with windows being implanted into the dial. The additional parts 4 to be implanted have two feet each, and corresponding holes for these feet are provided in the printed dial. If a part provided with a window is to be implanted, the dial is provided with an opening corresponding to the window.

Then the additional parts 4 are finished by caulking to fix them into the dial blank and the caulking is reinforced by injecting an adhesive agent.

The majority of such implanted dials are those in which letters are implanted. Usually the implanted letters are as many as 11 or 12 and the cost of the additional parts is rather high.

The implanting involves many steps, is difficult to automate and requires a number of hand operations. Moreover, implanting by hand is a very delicate operation and the workmen who perform it must be highly skilled.

Figures 4(1) and 4(2) illustrate a known process for coining a dial. The same process as explained above in relation to the printed dial is followed in fixing feet to the base, providing design, plating and coating.

Then by coining with a press die, the letters are raised as shown by Figure 4(1).

The raised letters are finished by a diacut, as shown in Figure 4(2), and the plating and printing on the diacut surface of the raised letters terminates the whole process for producing the coined dial, in which the dial and the letters are integrally formed.

Compared with the implanted dial, the coined dial does not require high skill in forming letters on a dial blank.

The coined dial, however, has two major defects:

First, since the production of metal dies for forming the raised letters is very expensive, coining is only suitable where the number of articles to be produced is large.

Secondly, there is a limitation on the variety of designs which can be provided by coining, because, since the dial and the letters are integral, it is not possible to perform a diacut finish on letters of complicated design.

The object of the present invention is therefore to provide an inexpensive method of manufacturing various kinds of watch dials in small quantities.

In one embodiment of the present invention, a photosensitive resin monomer layer of a predetermined thickness is therefore inserted between a base plate of a watch dial and a resin mould provided with the desired design surface of the watch dial so that the photosensitive resin monomer layer is given a dial surface portions of which are convex or concave. The photosensitive resin monomer layer is then hardened by irradiating its surface with ultraviolet radiation (UV radiation) which has passed through the resin mould. After that, by removing the resin mould, the photosensitive resin layer on which the surface design of the resin mould has been printed is formed on a base plate. Subsequently, a thin metallic layer is formed on the dial surface of the photosensitive resin layer by a dry or a wet process, so that a desired watch dial is produced.

One of the advantages of watch dials obtained by the method described in the previous paragraph is that a number of different dial surfaces can be produced with one apparatus merely by respectively using different resin moulds. Further, the UV resin can be hardened within a short time by the use of simpler equipment than that required for a conventional machining process. Therefore, it is easy to mechanise and automate the process, and a manufacturing line wherein respective processes are directly connected to each other can be achieved. Another advantage is that the variety of watch dials which can be produced is increased. That is, by preparing one master, a resin mould which can be used in the method of the present invention can be easily produced by casting and subsequent thermal polymerization, for example. Further, by using the master repeatedly, a large number of resin moulds can be produced so that, by using one master repeatedly,a large number of dial display portions can be produced.

As will be appreciated, the cost of making the master is insignificant, since a large number of watch dials can be produced by the use of resin moulds produced from one master. Further, designs can now be obtained which have not been practicable previously because of the numerous processes of the conventional manufacturing method used to make watch dials.

Manufacture of watch dials according to the present invention will be described in detail hereinafter merely by way of example.

Example I

A base plate 10 of 20/100 mm thickness is formed by stamping out steel material, as shown in Figure 5(1).

In the conventional method of making watch dials, the material of the base plate is restricted to nickel-copper alloy and to brass which has been specifically tempered to improve its characteristics. On the other hand, in the method of the present invention, the material of the base plate 10 is not so restricted and many kinds of material can be used. This greatly reduces the cost of the base plate 10. For instance, nickel-copper alloy used in the conventional base plate can cost more than three times as much as steel.

Next, as shown in Figure 5(2), feet 12 are fixed to the base plate 10 by resistance welding. When resistance welding, the surface 10a of the base plate 10 to which the feet 12 are fixed is distorted so that projections of 1/100 to 2/100 mm in thickness can occur in the opposite surface 10b too. But these distortions are insignificant, since the layer 15 of a photosensitive resin monomer is formed on the surface 10b of the base plate 10 in the next process, as shown in Figure 5(3). In the conventional method, when the feet 12 are fixed by resistance welding, the projections produced on the base plate from such resistance welding must be removed so as to produce an even surface, but this is unnecessary in the method of the present invention. Thus, an adequate amount of XFP 700 photosensitive resin produced by Asahi Kasei Co. is applied to the surface 10b of the base plate 10 to form the layer 15 and a transparent or semi-transparent CR-39 resin mould 14, which is provided with a desired under surface design having a plurality of convex and concave portions is placed on top of the layer 15. The thickness of the photosensitive resin monomer layer 15 may be 5/100 mm, the layer 15 being inserted between the base plate 10 and the resin mould 14 in such a way as to exclude air.

Next, the photosensitive resin monomer layer 15 is cured by directing ultraviolet radiation (UV radiation) of 20 mW onto the top surface 14a of the resin mould 14 for 30 seconds so that this radiation passes through the resin mould 14 and irradiates the upper surface 15a of the layer 15 whose design depends upon that of the resin mould 14. The photosensitive resin of the layer 15 is selected to provide good mould release characteristics with respect to the resin mould, good adhesive properties with respect to the base plate 10, good adhesive properties with respect to a subsequently applied thin metallic layer 16, and chemical resistance to coating solvents used in a subsequent coating process. The material of the resin mould 14 is selected to enable the resin mould to be easily produced (e.g. by coating and thermal polymerization) to be resistant to reaction with the photosensitive resin used, to give good mould release characteristics from the cured photosensitive resin and to give high transmittance of the ultraviolet radiation whose wavelength is about 365 nm.

A method of forming the resin mould 14 will now be described. First, a master is formed of metal, and a casting resin is cast between the metallic master and a glass plate, the resin is cured by thermal polymerization and is subsequently taken off the metallic master and the glass plate so as to complete the production of the resin mould. The metallic master can be used repeatedly, and many resin moulds can be produced from one metallic master. An acrylic resin suitable for casting, a transparent silicone rubber resin suitable for casting, as well as CR-39 resin, can be utilized for the resin mould.

Next, when the resin mould 14 is removed after the layer 15 has been cured by photopolymerisation, the surface 15<u>a</u> of the photosensitive resin layer 15 is uneven by reason of having been given the design of the mould surface of the resin mould 14 as shown in Figure 5(4). The adherent properties of the photosensitive resin of the layer 15 with respect to the base plate 10 can be improved by adding an adhesive of good metallic adherence to the photosensitive resin. In order to improve the adherence further, the adhesive of good metallic adherence may be coated onto the base plate 10 after the feet 12 have been fixed by welding with the result that the adhesive in a half-cured state reacts on the photosensitive resin so as to provide adequate adhesion strength. After that, ultraviolet radiation of 20 mW and 365 nm is directed onto the surface 15a of the photosensitive resin for five minutes, so that the photosensitive resin layer 15 is completely polymerization cured.

Next, metallizing is carried out on the surface 15a of the photosensitive resin layer 15 by a wet plating method or by a dry plating method so as to produce the thin metallic layer 16, as shown in Figure 5(5). In the case of the wet plating method, an electroless Ni plating is the most suitable having regard to the appearance of the plating layer 16 and the adherence of the plating layer 16 to the photosensitive resin layer 15. A preliminary treatment is carried out prior to such plating, by which the resin is dispersed in a tin chloride solution (1% solution) for one minute, washed with water, and then dispersed in a palladium chloride solution for one minute, and is subsequently washed with water and dried.

After the above-mentioned preliminary treatment, the resin which has been so prepared is dispersed in an electroless Ni-P alloy plating S-680 produced by

Kanizen Co.) at a temperature 50°C for one minute. Next, as Ni-P plating and a final plating (Au-P, Ag-P and so on) are conducted thereon by an ordinary electrolytic plating method.

A deposition process and a sputtering process can be employed as a dry plating process. In particular, a low-temperature sputtering process is the most suitable for metallizing the surface of the resin. For instance, in the case of a gilt coloured metallizing process, Ni of 1000 Å is sputtered by a low temperature sputtering apparatus, and then Au of 500 Å tp 1000 Å is sputtered, so that the desired gilt colour can be obtained depending on the thickness of Au.

After metallizing, the metallic layer 16 is coated with a transparent coating layer 13, the upper surface of the transparent coating layer 13 is printed, and the dial is punched out so that a printed dial provided with a required surface design is provided as shown in Figure 5(6).

The above-mentioned example, relates to a printed dial provided with a surface design having a plurality of both convex and concave portions. However, a dial having one or more concave and/or convex portions, and optionally provided with one or more indicia such as letters, symbols, pictures and marks and/or with at least one hole or window, can be produced in the same way as that of the above example by forming a suitable resin mould.

The method described in Example I has the following advantages:-

(1) The amount of both labour and equipment is reduced and a manufacturing line can be easily established.

(2) A number of different kinds of dials can be economically produced in small quantities.

(3) No large apparatus is required.

(4) The time taken to manufacture the dials can be greatly shortened.

(5) Factory space can be greatly reduced.

(6) The variety of design of the dials can be increased.

(7) Indirect costs can be reduced by simplifying the manufacturing process.

(8) The method does not require special skills.

Example II

Figures 6(1) to 6(5) illustrate a second embodiment of this invention.

First a transparent film 26 of polyethylene terephthalate (PET) resin is put on a mask 25 which has a transparent part corresponding to the radially inner part of the dial and a black part corresponding to the periphery thereof. Then a spacer 27 which is as thick as the dial, is provided around the periphery of the transparent PET film 26. An appropriate quantity of a photosensitive plastics monomer 28 (XFP 700 by Asahi Kasei Co. Ltd) is applied near to the centre of the PET film 26

(Figure 6(1)). The photosensitive plastics monomer 28 must not include foams and so it is desirable to effect a vacuum de-aeration after applying the monomer 28, if possible.

A die 40, formed of a plastics material marketed as CR-39, is provided with an uneven under surface design 40a incorporating both convex and concave portions and is also provided with concave letter mould portions 40b. The die 40 is placed so as to sandwich the photosensitive plastics monomer 28 between the die 40 and the PET film 26. At this time, care must be taken to prevent air from entering between the PET film 26 and the plastics die 40. To ensure that air is excluded it is desirable to place the plastics die 40 in a vacuum of $10^{-2}$ torr.

Then, ultraviolet radiation (UV) having a wavelength of 350 to 400 nm is applied to the photosensitive monomer 28 from the side of the mask 25 so as to harden the photosensitive monomer 28 (Figure 6(2)). The photosensitive monomer 28 is hardened by less than 5 seconds' application of UV of 150mW.

The photosensitive plastics material used in this embodiment is selected by taking account of factors such as releaseability from the plastics die 40 which is used, adhesion properties with respect to a metalizing thin layer which is to be provided on the photosensitive plastics material, corrosion resistance with respect to a paint solvent in a subsequent process, and so on.

The material of the plastics die 40 is selected with respect to the ease with which one can form the die 40 (e.g. the applicability of a casting or thermal polymerizing method to transfer designs from a master by means of which the CR-39 die 40 is formed), non-reactivity to the used photosensitive plastics 28, releaseability from the hardened photosensitive plastics 29, and so on. Additionally, if the UV mentioned in Example III below is used to harden the photosensitive plastics 28 by application thereto through the plastics die 40, the material of the die 40 is required to have high ultraviolet light transmittance for ultraviolet light having a wavelength of 350 to 400nm.

The method of making the plastics die 40 is explained with reference to Figures 9(1) to 9(3).

First, as shown in Figures 9(1), a metal master 41 is formed having implanted letters 44 or other indicia. The metal master 41 is equivalent to the desired watch dial and may be made in a currently used process for making a watch dial at a very low cost.

Then, as shown in Figure 9(2), a casting plastics monomer 40c (CR-39) is injected into a space defined by a spacer 47 which extends between the metal master 41 and a glass member 43, and the monomer is then set hard by thermal polymerization. After the plastics monomer has been hardened, the metal master 41 and the glass member 43 are removed to obtain the plastics die 40, as shown in Figure 9(3).

The metal master 41 can be used repeatedly so as to produce a large number of plastics dies from one master.

Besides CR-39, a casting type acrylic plastics material, a transparent silicone rubber plastics material suitable for casting and the like can also be used as the material of the plastics die 40.

Referring now to Figure 6(3), after the application of UV is finished, the photosensitive plastics layer is released from the plastics die 40, and then the photosensitive plastics monomer 28 which remains unhardened is removed by washing with a specific developer which is preferably sodium borate ($Na_2B_4O_7$).

The surface 29a of the photosensitive plastics layer 29 on which the design is transferred from the plastics die 40 is metalized by means of a metallic thin layer 31, as shown in Figure 6(4). This metalization can be effected either by wet plating or by dry plating. In the case of wet plating, an electroless Ni plating is the best so far as the appearance of the plating layer and the adhesiveness between the plating layer and the photosensitive plasitcs material is concerned.

Before plating, a surfaca preparation is preferably performed including dipping the surface 29a into a stannous chloride solution (density: 1%) for one minute, washing it with water, dipping it into a palladium chloride solution (density: 5% to 10%) for one minute, and washing it with water followed by drying.

After the above surface preparation, the material is plated by dipping it into an electroless Ni-P alloy (marketed as S-680 by Cannizen Co) in which it is maintained at 50°C for one minute. The thus formed Ni-P layer contains 8wt% of P and may be as thick as approximately 500Å. The electroless Ni-P plating layer is preferably as thin as possible, since the thinner the layer, the better is its adhesion to the photosensitive plastics material. The most desirable thickness of the electroless Ni-P alloy plate is between 400 and 600Å.

Instead of an electroless Ni-P alloy plating, a Ni-B alloy plating may be used.

The surface is then subplated with an electrolytic Ni-series material, which subplating is necessary for the subsequent final plating with Ag, Au and so on. That is, because of problems with respect to throwing power, it is almost impossible to provide the final plating directly on the electroless Ni-series plating. The reason for this is that an electroless Ni-P alloy plating including P has an electric resistivity ten times as high as that of an electrolytic Ni plating, and that the electroless Ni-P plating is made very thin. This problem is particularly severe when the final plating material is Ag.

Furthermore, the material of the electroless subplating should be unlikely to diffuse into the final plating by heat. For example, in the case where the final plating is Ag and the subplating is Cu, Cu diffuses into Ag, resulting in the discoloration of the Ag plating.

As regards throwing power, the use of a wet bath is suitable for electrolytic Ni-series plating.

The constituents and conditions of the electrolytic Ni plating may be as follows:

| | |
|---|---|
| nickel sulfate hexahydrate | 225g/1 |
| nickel chloride hexahydrate | 40g/1 |
| boric acid | 25g/1 |
| brightener | 5g/1 |
| pH | 4.3 |
| fluid temperature | 50°C |
| electric current density | $1A/dm^2$ |

Under the above conditions, an electrolytic Ni-series plating may be provided such that the thickness of the plating layer including the electrolytic Ni-series plating, and the electroless Ni-series plating is between 1,500Å and 3,500Å. The highest and the lowest ends of the above range are determined with respect to the adhesion between the photosensitive plastics material and the metal film, and the throwing power of the final plating, respectively.

In the above description, an electrolytic Ni plating is referred to merely by way of example. However, a single metal plating or an alloy plating of Co or Fe are also available as the subplating. Moreover, examples of alloy plating are Ni-Co plating, Fe-Ni plating, Ni-Pd plating and so on.

A final plating is provided on the electrolytic Ni-series plating. The material of the final plating is usually selected from Ag, Au, black nickel and the like and the thickness thereof is preferably approximately 500Å which allows the shade of colour to appear effectively. In Figure 6(4), the plating layer 31 includes three layers of electroless Ni deposition, Ni subplating and the final plating.

Finally, painting and printing are provided and thus a finished watch dial is obtained as shown in Figure 6(5), which is provided with a transparent protective layer 12.

Figure 8 is a plan view of the watch dial of Example II.

Example III

Another embodiment of this invention is described in detail below with reference to Figures 7(1) to 7(5).

First, a base plate 51 is formed by punching out a steel material having a thickness of 20/100mm. In general, an available material for the base plate 51 is a nickel-copper alloy or brass whose quality is specially modified to reduce material defects. However, it is not necessary to select a substantially modified material for the base 51 and generally available materials may also be used. Consequently, the material cost is largely reduced. For example, if steel is used, the cost is less than one quarter of that where a nickel-copper alloy is used.

Then feet 52 are fixed to the base 51 by the resistance welding method. At this time, the obverse of the base 51, where the feet 52 are fixed, is transformed, that is, projections as high as 1/100 to 2/100mm are produced. However, the projections do not raise any problem if the thickness of a photosensitive plastics layer 59 which is to be subsequently formed on the obverse of the base 51 is more than 8/100mm. Accordingly, in contrast to the prior art, an additional process is not necessary to remove the projections on the obverse of the base.

Next, an adhesive agent is applied to the obverse of the base plate 51 to improve the adhesion between the base plate 51 and a photosensitive plastics curing layer which is formed in the next process. The used adhesive agent is an isopropylalcohol solution containing 2wt% of methacryloxy propyl trimethoxy silane, 2 wt% of tetramethoxy silane and 1wt% of tetraoctyloxy titanium $(Ti(OC_8H_{17})_4$. The said adhesive agent is sprayed over the obverse of the base and is heated at a temperature of 150°C for one hour to make a film of the adhesive agent so that the film is interlocked with the obverse of the base. In order to improve the interlock therebetween, it is preferred to roughen the obverse of the base by giving it a satin finish, for example. The thickness of the adhesive agent is about 500Å.

Of the constituents of the adhesive agent, γ-methacryloxy propyl trimethoxy silane

$$\left( CH_2 = \underset{\substack{| \\ CH_3}}{C} - \underset{\substack{\| \\ O}}{C} - O(CH_2)_3\ \ Si(OCH_3)_3 \right)$$

has the function of bonding the adhesive agent to the photosensitive plasics material. To be more concrete, γ-methacryloxy propyl trimethoxy silane is a hydrolytic silicon compound having an ethylene unsaturated substituent group, and the unsaturated group bonds chemically with the photosensitive monomer by light reaction and so that a strong adhesion therebetween is achieved. Besides γ-methacryloxy propyl trimethoxy silane, there can also be used other hydrolytic compounds having ethylene unsaturated substituent groups such as vinyl triethoxy silane

$$(CH_2 = CH - Si(OC_2H_5)_3).$$

Another constituent of the adhesive agent, tetramethoxy silane, has the function of bonding the adhesive agent to the metal base. For that purpose, another tetraalcoxy silane compound such as tetraethoxy silane or tetrapentoxy silane is applicable.

The tetraoctyloxy titanium is catalytic through the hydrolysis of the hydrolytic compound having an ethylene unsaturated substituent group and a tetraalcoxy silane compound. For such a catalytic function as above, a tetraalcoxy titanium compound such as tetrabutoxy titanium or tetrahexyloxy titanium, in addition to tetraoctyloxy titanium, an aqueous acid such as HCl and a mixture of an aqueous acid and organic catalysts such as alcohol, ketone or ester are available.

On the adhesive agent coated surface of the base plate 51 there is applied an appropriate amount of XFP 700 photosensitive plastics monomer 58 made by Asahi Kasei Co., Ltd as shown in Figure 7(1). The photosensitive plastics monomer 58 applied to the base 51 should be degassed, preferably by vacuum deaeration, the degree of vacuum being $10^{-2}$. torr.

Next, a CR-39 plastics material die 6o having a desired under surface design and depressed figures is pressed onto the photosensitive plastics monomer 58 so that the plastics die 60 and the base plate 51 sandwich the photosensitive plastics monomer 58 therebetween so as to maintain the thickness thereof as 10/100mm. At this time, in order to prevent air from entering between the base plate 51 and the plastics die 6o, the vacuum deaeration referred to above is performed.

Then, as illustrated in Figure 7(2), ultraviolet light (UV) having a wavelength of 350 to 400nm is then directed onto the upper surface of the plastics die 60 to cure the photosensitive plastics monomer. The strength of the ultraviolet light is 150mW and the application thereof is for less than 5 seconds. When the photosensitive plastics is cured, the photosensitive plastics chemically bonds to the adhesive agent and consequently the photosensitive plastics layer bonds to the base plate through the intermediary of the adhesive agent.

The photosensitive plastics monomer 58 may be constituted by the same material as was described above in Example II.

The material of the plastics die 60 is required to have a good transmittance for ultraviolet light of a wavelength of 350 to 400nm in addition to the necessary properties mentioned in Example II so that the curing of the photosensitive plastics monomer 58 is achieved by applying ultraviolet light thereto through the plastics die 60. In this embodiment, besides CR-39, the casting acrylic resin, a transparent silicone rubber resin and so on may also be used.

After curing the photosensitive plastics material, the plastics die 60 is removed and what is equivalent to a master, in which the photosensitive plastics layer 59 having an obverse to which the design of the plastics die 60 has been transferred, is formed on the base plate 51 as shown in Figure

7(3). The thickness of the photosensitive plastics layer 59 is 10/100mm.

It should be noted that the thickness of the photosensitive plastics layer 59 has a great effect on the metal film which is to be formed thereon in the later process. That is, if the thickness is less than 8/100mm, the metal film partially blisters and also the quality of the metal material has poor durability even if the material is satisfactory at first. For example, if it is subjected to a thermal shock of more than 100°C, the metal film partially blisters. If, however, the thickness of the photosensitive layer is greater than 8/100mm, blistering of the metal film is avoided and the metal film is resistant to thermal shocks of up to 150°C.

The table below shows the result of an experiment on the correlation of the thickness of the photosensitive plastics layer and the incidence of the blistering of the metal film, the latter comprising an electroless Ni deposit of up to 500Å in the thickness, an electrolytic Ni subplating of up to 2,000Å in thickness, a final Ag plating of up to 500Å in thickness, and a coating layer of up to 500Å in thickness.

| Thickness \ Incidence of Blistering | Finished article | Thermal Shock |
|---|---|---|
| 5/100mm | 50% | 70% |
| 8/100 | 0 | 0 |
| 20/100 | 0 | 0 |

In the above table, the columns headed "Finished article" and "Thermal shock" respectively show the incidence of blistering of the metal film at the time when the finished watch dial is originally manufactured and after a perfect article has been maintained at a temperature of 150°C for 30 minutes.

Ultraviolet light having a wavelength of 350 to 400nm is then applied to the photosensitive plastics layer 59 to whose surface the design has been transferred so as to sufficiently harden the photosensitive plastics 59.

After hardening, the surface with the transferred design is metalized.

It is first subjected to a surface treatment to provide the catalytic nucleus for the electroless Ni deposition by using a surface treatment solution produced by Hitachi Kasei Co. as follows. The material is immersed in a 20% HCl solution for the first 2 minutes, and then in a sensitizing agent

(HS-101B) for the next 5 minutes, and then after treatment with an adhesion acceleration agent (ADP-201) for 3 minutes, it is washed with water again.

After the above surface treatment, the material is dipped into an electroless Ni-P alloy (S-680 by Cannizen Co.) at a temperature of 50°C for 1 minute. As a result, an Ni-P layer whose content of P is 8wt% is obtained having a thickness of about 500Å.

Then, an electrolytic Ni plating is superimposed on the electroless Ni-P layer having a thickness of 2,000Å by using the same plating solution under the same conditions as described in Example II.

The final plating of Ag is deposited on the electrolytic plating to a thickness of 500Å. In Figure 7(4) a plating layer 61 is shown which consists of three layers, namely an electroless Ni plating layer, a Ni subplating layer, and a final plating layer of Ag.

On the very top of the so-formed three plating layers, a transparent protective layer 62 is formed by spraying an isopropyl alcohol solution containing 2wt% of tetramethoxy silane and 1wt% of tetraoctyloxy titanium $Ti(OC_8H_{17})_4$ and by heating at a temperature of 150° C for 15 minutes. By the above operation, a transparent protective layer having a thickness of 300 to 500Å is formed. This protective layer is so thin that it does not affect the appearance of the finished dial.

Also, the protective layer, which is very dense, prevents the discoloration of the final plating layer.

The tetramethoxy silane in the above solution is a hydrolytic organic silicon compound and contributes to the making of the film dense by being hydrolyzed with a catalyst of tetraoctyloxy titanium. Other hydrolytic organic silicon compounds other then tetramethoxy silane may also be used.

Usually, in forming the protective layer to prevent the chemical discoloration of the final plating, there is a problem that the protective layer may affect the appearance of the finishea dial. In this embodiment of the present invention, if the protective layer is thicker than 1μm, the thickness of the layer becomes uneven on and around the letters, especially at a convex or concave corner of any indicator members provided, and consequently the appearance of the dial suffers. If the protective layer is thinner than 1μm, the unevenness of the thickness is eliminated but interference colour appears. Accordingly, the protective layer should be not thicker than 800Å, which thickness is free from interference colour and still prevents the discoloration of the final plating. However, the plastics protective layer used in a known watch dial loses the ability to prevent the discoloration when the layer is thinner than 800Å and consquently the latter cannot be used.

After forming the protective layer, minute scales and so on are printed on the dial.

Finally, the external periphery of the dial and the centre hole are punched out and the watch dial of this embodment is obtained, as shown in Figure 7(5).

The description so far has been concerned with a method of making a watch dial in which the surface of the base and the letters (or other indicia) are of the same color. However, a method in which the colour of the base and of the letters (or other indicia) is different is described below.

The same processes as in the above description are followed until the electrolytic Ni plating is completed. Before the final plating, an Au plating for colouring the letters is deposited on the electrolytic Ni plating layer.

Then the portions to become the letters are covered by resists. In order to provide resists in certain places only,a screen printing method may, for example, be employed.

Next, an Ag plating for colouring the base is deposited.

After chemically separating the resists, a watch dial is obtained in which the letters are of the colour of Au and the designed base plate is of the colour of Ag.

The following is a description of a process for manufacturing a watch dial in which a mat coating or a colour coating is provided on the part of the dial which is not provided with the letters (or other indicia).

After the final plating and the transparent protective layer have been formed by the steps described in Example III, the letters (or other indicia) are coated by the resists.

Then, the desired mat coating or the colour coating is spread over the whole surface of the watch dial.

By chemically separating the resists by dissolving, the mat coating or the colour coating on the resists is removed, and the part of the watch dial which does not have the uneven portions provided with letters or other indicia, is provided with the mat coating or the colour coating.

The finished watch dial can be proved to be free from liability to deteriorate in quality by subjecting it to certain examinations such as a thermal shock test (150° for 30 minutes), a thermal cycle test (repetition of 60°C for 30 minutes and -20°C for 30 minutes) and a fadeometer test (wet atmosphere 200H). Accordingly, a watch dial in accordance with this invention is equivalent to a conventional watch dial both in appearance, quality and functionally.

As mentioned above, by forming the uneven portions such as the surface design, letters, marks and so on, all of which are convex and/or concave, by photopolymerization of the photosensitive plastics material and then processing its surface by metal plating, some of the manufacturing processes conventionally followed are combined into one single process, largely reducing the number of the manufacturing processes. Also, the process in accordance with the present invention is very simple. Thus, by eliminating the troublesome processes which make the mechanisation and the automation of the manufacture of watch dials difficult, the present invention permits automation of watch dial manufacturing with light equipment and enables a single-line factory system to be realized, resulting in a substantial reduction of cost.

Moreover, the delivery time for producing the finished watch dial is substantially shortened.

The present invention enables other advantages to be obtained such as the reduction of factory space, the reduction of indirect charges as a result of simplification in the transportation of products, and the ability to dispense with specially trained workers.

The designs of the watch dials can be easily varied when using the present invention. In the present invention, one master which is equivalent to the desired watch dial may be made and with such a master a plurality of different plastics moulds or dies may be formed. By repeatedly using these plastics moulds many watch dials may be produced. Since the original master results in the production of a larger number of watch dials through the use of the said plastics moulds, the cost of making the master can be relatively neglected.

This invention also enables certain designs to be achieved which cannot be obtained in the prior art because of the limitation of the number of manufacturing processes.

Furthermore, in the case of the present invention, a surface design may, for example, be formed by utilizing a natural material such as a leaf as a master.

# CLAIMS

1. A timepiece dial comprising a photosensitive layer having a surface at least part of which is uneven by reason of having one or more convex or concave portions and which has been photopolymerised, and a metal layer which covers at least the said uneven part.

2. A dial as claimed in claim 1 in which the whole of the photosensitive layer has been photopolymerised.

3. A dial as claimed in claim 1 or 2 in which the whole of the said surface is covered by the said metal layer.

4. A dial as claimed in any preceding claim in which the said uneven part is formed with at least one indicium or aperture and/or with a design.

5. A dial as claimed in any preceding claim in which the photosensitive layer is provided on a metal base plate.

6. A dial as claimed in claim 5 in which an adhesive agent is provided between the metal base plate and the photosensitive layer.

7. A dial as claimed in any preceding claim in which the dial comprises a transparent coating layer which covers at least the said part of the said surface.

8. A dial as claimed in claim 7 in which the surface of the transparent coating layer remote from the said surface of the photosensitive layer is printed.

9. A dial as claimed in claim 6 in which the adhesive agent is a mixture of a hydrolytic silicon compound having an ethylene unsaturated substituent group, hydrolytic tetraalcoxy silane and a catalytic component.

10. A dial as claimed in claim 9 in which the catalytic component is tetraalcoxy titanium or an aqueous acid.

11. A dial as claimed in any preceding claim in which the thickness of the photosensitive layer is 8/100mm or more.

12. A dial as claimed in any preceding claim in which said metal layer comprises an Ni group electroless plating layer, an electrolytic subplating layer and a final plating layer.

13. A dial as claimed in claim 12 in which the thickness of the Ni group electroless plating layer and of the electrolytic subplating layer is in the range 1,500Å to 3,500Å.

14. A dial as claimed in claim 12 or 13 in which said electrolytic subplating layer is constituted by a plating of a single metal.

15. A dial as claimed in claim 12 or 13 in which said electrolytic subplating layer is constituted by an alloy plating of Ni, Co or Fe.

16. A dial as claimed in any preceding claim in which the colour of said uneven part and the colour of the metal layer are different from each other.

17. A dial as claimed in claim 7 in which the transparent coating layer is constituted by a layer not thicker than 800Å which is superimposed on said metal layer.

18. A dial as claimed in claim 17 in which said transparent coating layer is a film containing at least one hydrolytic silicon compound.

19. A dial as claimed in any preceding claim in which the photosensitive layer has a part other than the said uneven part which is provided with a colour coating or with a mat coating.

20. A method of making a timepiece dial comprising providing a photosensitive layer with a surface at least part of which is uneven by reason of having one or more convex or concave portions, photopolymerising at least the said uneven part, and covering at least the said uneven part with a metal layer.

21 . A method as claimed in claim 20 in which the whole of the photosensitive layer is photopolymerised.

22. A method as claimed in claim 20 or 21 in which the whole of the said surface is covered by the said metal layer.

23. A method as claimed in any of claims 20-22 in which the said uneven part is formed with at least one indicium or aperture and/or with a design.

24. A method as claimed in any of claims 20-23 in which the photosensitive layer is provided on a metal base plate.

25. A method as claimed in any of claims 20-24 in which the polymerisation is effected by ultraviolet light.

26. A method as claimed in claim 25 in which the ultraviolet light is directed onto the said layer by way of a transparent or semi-transparent mould which has been used to form the said surface.

27 . A timepiece dial substantially as hereinbefore described with reference to and as shown in Figures 5-8 of the accompanying drawings.

28. A method of making a timepiece dial substantially as described in any of Examples I - III.

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Applicant:
Kabushiki Kaisha Suwa Seikosha (Japan), 4-1 2-chome Nishi-shinjuku, Shinjuku-ku, Tokyo, Japan.

Inventors:
Masami Kasai, 3-3-5 Owa, Suwa-shi, Nagano-ken, Japan.

Masao Kanai, 3-3-5 Owa, Suwa-shi, Nagano-ken, Japan.

Akira Okubo, 3-3-5 Owa, Suwa-shi, Nagano-ken, Japan.

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J Miller & Co, Lincoln House, 296-302 High Holborn, London WC1V 7JH.

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