

A COLOURED ARTICLE

This invention relates to coloured articles, for example, exterior parts, spectacle frames, stationery, personal ornaments, accessories, etc. and, more specifically, it relates to coloured articles exhibiting various colours by the interference of light.

Heretofore there has been no intentional control of light interference to produce exterior visible tones or colours in watches, miscellaneous goods, electrical products, etc. That is, colours such as red, orange, yellow, green, blue, purple blue (indigo) and purple for exterior use have only been obtained using pigmented resins or the like, or by applying paint or by plating articles of metal or resin material.

Accordingly, colours obtained by the known techniques are, so to speak, those of the materials per se and lack clearness of transparent feeling. In addition, in the case of painting or plating, there has been a problem of close bondability of painted films or plated layers to the material of the article, which may cause drawbacks of peeling or abrasion.

The present invention seeks to provide a coloured article exhibiting bright tones of transparent feeling by the interference of light with good reproducibility

and with excellent abrasion and corrosion resistance.

According to one aspect of the present invention, there is provided a coloured article comprising a light permeable coating layer made of a mixture consisting of SiC and SiO₂ with a thickness of 200 to 3000 Å, the SiO₂ being present in an amount of 5 to 80% by weight, the coating layer being formed on a reflection surface of a pre-determined reflectance.

According to another aspect of the present invention, there is provided a coloured article comprising a light permeable coating layer made of a mixture consisting of Si₃N₄ and SiO₂ with a thickness of 200 to 4000 Å, the SiO₂ being present in an amount of 5 to 80% by weight, the coating layer being formed on a reflection surface of a pre-determined reflectance.

Preferably the coating film is formed by vapour deposition, sputtering or ion plating.

The reflection surface may comprise a plurality of surfaces different from each other in their distance from or angle relative to the frontmost surface of the article.

In one embodiment the article is of non-metallic material such as synthetic resin or ceramic and the reflection surface is a primer layer. In another embodiment the article is of metal and the reflection surface is formed by surface treatment.

The reflection surface may be formed as a curved surface.

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

Figure 1 is a diagram to explain the principle of the present invention;

Figure 2 is a cross-section of a portion of one embodiment of a watch case to which the present
5 invention has been applied;

Figure 3 is a cross-section of a portion of another embodiment of a watch case to which the present invention has been applied;

Figure 4A is a plan view of a further embodiment
10 of a watch case to which the present invention has been applied;

Figure 4B is a cross-sectional view taken along line IV-IV in Figure 4A; and

Figures 4C and 4D are, respectively, enlarged
15 cross-sectional views of portions of the watch case of Figure 4A.

The principle of the present invention lies in producing colours by light interference which will be explained with reference to Figure 1. A reflection
20 surface 2 having a predetermined reflectance is formed on an article 1 as a primer layer. The article 1 may be made of plastics, metal, ceramic, etc. with no particular restriction, a mirror-like grinding treatment being applied in the case of metal to form the
25 reflection surface 2 and primer treatment with high

reflectance being applied by, for example, a plating technique in the case of plastics or ceramic. A light permeable coating layer 3 made of a mixture comprising a nitride, oxide, carbide, etc. of Si is formed on the reflection surface 2. The coating layer 3 has a thickness such as to be capable of producing a visible colour or colours by the interference of light.

In Figure 1, instant light is indicated by I_1 , I_2 , the thickness of the light permeable coating layer 3 is indicated by t , reflection light is indicated by I , the angle of incidence of the incident light I_1 , I_2 is indicated by α , refractivity or refractive index of the light permeable coating layer 3 is indicated by μ , and the angle of reflection is indicated by β . The interference between the reflection light $I_1.M_1$, I at a

front surface AB of the light permeable coating layer and the reflection light I_2 . M_2 , M_3 , M_1 , I from a rear face CD of the light permeable coating layer can be represented as: $PM_3 + M_1M_3 = PO = M_1O \cos \beta = 2t \cos \beta$,

5 which is converted into an optical path length in air by multiplying the refractivity μ into $2\mu t \times \cos \beta$.

Since the interference of light occurs such that they offset each other to obtain a dark condition when the difference between the optical paths is an odd number

10 multiple of the half wavelength, while strengthening each to obtain a bright condition when it is an even number multiple of the half wavelength, considering the phase deviation of $1/2$ wavelength upon reflection at the surface CD. Assuming n is a possible integer and λ is

15 the wavelength, the bright condition can be expressed as: $2n \times \lambda/2 = \mu t \cos \beta + \lambda/2$, i.e., $\mu t \cos \beta = \lambda/4 (2n-1)$, while the dark condition can be expressed as $(2n+1)\lambda/2 = 2\mu t \cos \beta + \lambda/2$, i.e. $\mu t \cos \beta = \lambda/4 (2n)$. If the thickness t of the light permeable coating

20 layer 3 and the refractivity μ are known, the colour or wavelength produced by the interference of visible light can be determined. Further, it is also possible to determine the thickness t of the light permeable coating layer 3 in accordance with the wavelength of a required

25 colour. Further, if the angle of incidence changes, the

tone or visible colour varies in a delicate manner depending upon the direction of viewing. Since the parallellism of the surfaces of the light permeable coating layer 3, spectral reflectance property inherent
5 to the substance of the light permeable coating layer, the purity of the substance of the light permeable coating layer, difference in absorption level, birefringence in which light is separated with deviated optical oscillation faces depending on the direction of
10 crystallisation in the substance of the light permeable coating layer, refraction phenomenon, etc. are also involved, an explanation based solely on the principles of light interference is too simple.

Based on the principle as described above a
15 desired interference colour can be produced by selectively interfering light including a desired wavelength from those of incident light (natural light or white light).

Further, the interference colour, or wavelength, can
20 be determined by controlling the thickness of the light permeable coating layer as described above, as well as by making the light permeable coating layer as a multi-layered film, each layer comprising a different substance and selecting the substance forming each of
25 the layers, setting the order of the layers and

controlling the thickness of each of the layers.

5 An interference colour can be selected by
controlling the thickness of the light permeable coating
layer and the material of the light permeable coating
layer thereby obtaining a clear tone of transparent
feeling such as red, orange, yellow, green, blue, purple
10 blue (indigo) and purple by way of interference of
light. Exterior casings or accessories can, therefore,
be produced with a high quality feeling.

EXAMPLES

15 **EXAMPLE 1**

After applying a mirror finish to a surface of an
article by grinding, plating or the like in the case

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where the article is of metal, or after applying a primer treatment of high reflectance such as by plating in the case where the article is of resin or ceramic, a light permeable coating layer comprising a composite material consisting of SiC as the main ingredient and SiO₂ with an ingredient ratio from 5 to 80% by weight was coated on the surface. The light permeable coating layer was a transparent film of brown-red colour, and only light in a specific wavelength region was caused to interfere. The following are more specific illustrations of this.

EXAMPLE 1-1

After placing a flat plate made of polycarbonate (PC) resin in a sputtering device and reducing the pressure to a vacuum of about $(1.0-2.0) \times 10^{-3}$ Pa, argon gas was injected to a pressure of 6.0×10^{-1} Pa and chromium metal (for primer treatment) and a composite material containing SiC as the main ingredient and 20% by weight SiO₂ was used as a target.

Primary treatment was first applied to the plate by sputtering the chromium metal at a high frequency output of 8 Watts/cm² for 2 minutes and, thereafter, composite material of SiC-SiO₂ was sputtered at a high frequency output of 8 Watts/cm² for 8 minutes. As a result, it was possible to produce a chromium primer

layer to a thickness of 500 Angstroms and a light permeable coating layer of SiC-SiO₂ to a thickness of 1400 Angstroms on the flat plate, and a red interference colour was obtained over the entire area of the coated surface of the plate.

EXAMPLE 1-2

In the same manner as above, a chromium primer layer was produced with a constant thickness of 500 Angstroms, while the thickness of the light permeable coating layer of SiC-SiO₂ was changed by varying the sputtering time. Interference colours were obtained over the entire area of the coated surface of the plate, that is, blue interference colour at 600 Angstroms, yellow interference colour at 1200 Angstroms, purple blue interference colour at 1700 Angstroms and green interference colour at 1900 Angstroms of the thickness of the SiC-SiO₂ light permeable coating layer respectively. When the thickness of the light permeable coating layer was further increased, a red interference colour was obtained at 2300 Angstroms, but no interference was exhibited if the thickness was increased further.

As has been described above, light in a specified wavelength region, that is the interference colour, can be selected depending on the thickness of the light

permeable coating layer. In this case, the thickness of the light permeable coating layer and the selectivity of the wavelength region were varied with the ingredient ratio of SiO_2 in the composite material showing a
5 tendency that the change of wavelength region, that is the change in the interference colour, with the thickness of the light permeable coating layer was moderated with increase in SiO_2 content and the brightness of the interference was reduced.

10 In view of the relation with the brightness, the upper limit of SiO_2 was 80% and the maximum thickness of the light permeable coating layer showing an interference colour, which was blue, was 3000 Angstroms.

EXAMPLE 1-3

15 In the case where the light permeable coating layer was composed solely of SiC , the change of the wavelength region relative to the thickness became sharp, which was unfavourable since it was difficult to obtain an identical interference colour over the entire
20 area of the coated surface in relation to the distribution of the thickness of the light permeable coating layer upon its formation and there was also a problem with reproducibility. It was found preferable that SiO_2 is present in the composite material at least
25 in an amount greater than 5% by weight. In this case,

a clear blue interference colour was exhibited with a thickness of the light permeable coating layer of 200 Angstroms and interference colour changed as described above with increase in the thickness. Particularly, red
5 interference colours were obtained with increase in wavelength and blue purple interference colours were obtained with shorter wavelengths.

Although the light permeable coating layer was formed by sputtering in the above example, it is also
10 possible to use vacuum vapour deposition or ion plating in place of sputtering.

In the case of employing an electron beam as an evaporation source for both vacuum deposition and ion plating, a mirror-finished flat metal plate was placed
15 in a device, SiC-SiO₂ composite material with an appropriate ingredient ratio was placed in a crucible and vapour deposition or ion plating was applied under appropriate evaporating conditions to form a light permeable coating layer on the flat metal plate.

20 In the case of a flat plate made of resin material, two electron guns and crucibles were disposed in a single device, metal such as chromium was placed in one of the crucibles while SiC-SiO₂ composite material with an appropriate ingredient ratio was placed in the
25 other crucible. The metal was first evaporated by an

electron gun to form a primary layer on the flat resin plate and, thereafter, the SiC-SiO₂ composite material was evaporated to form a light permeable coating layer.

In this example, clear tones such as of red,
5 orange, yellow, green, blue, purple blue or purple could be obtained, the colour depending on the angle of view thereby obtaining a colour of an extremely highly decorative nature.

Further, the selectivity of the wavelength region
10 of the reflection light relative to the layer thickness was moderated by the addition of SiO₂ to SiC thereby enabling a given colour to be obtained with a high degree of reproducibility. Further, since the transparency of the light permeable coating layer was
15 increased by the addition of SiO₂, the tone became clearer with higher transparent feeling.

In addition, since SiO₂ was added to SiC, the problem of close bondability and impact shock resistance, and inherent drawback of SiC, could be
20 improved and an ornamental layer obtained which had from 1500 to 2400 Hv of micro Vickers hardness and, although somewhat inferior in hardness as compared with SiC alone, was sufficiently hard as an ornamental layer, with excellent abrasion and corrosion resistance because
25 of its carbide and oxide constitution.

EXAMPLE 2

After applying a mirror finish to a surface of an article by grinding, plating or the like in the case where the article is of metal or after applying primer treatment of high reflectance by plating or the like in the case where the article is of resin or ceramic, a light permeable coating layer comprising a composite material consisting of Si_3N_4 as the main ingredient and SiO_2 with an ingredient ratio of from 5 to 80% by weight was coated on the surface. The light permeable coating layer was a transparent brown colour and caused interference of light to produce a specific tone.

EXAMPLE 2-1

After placing a flat plate made of PC resin in a sputtering device and reducing the pressure to a vacuum of about $(1.0-2.0) \times 10^{-3}$ Pa, argon gas was injected to a pressure of 6.0×10^{-1} Pa, chromium metal (for primer treatment) and a composite material containing Si_3N_4 as the main ingredient and 20% by weight SiO_2 was used as a target.

Primary treatment was first applied to the plate by sputtering chromium metal at a high frequency output of 8 Watts/cm² for 2 minutes and thereafter a composite material of Si_3N_4 - SiO_2 was sputtered at a high frequency output of 8 Watts/cm² for 8 minutes. As a result, a

chromium primer layer with a thickness of 500 Angstroms was produced and a light permeable coating layer of $\text{Si}_3\text{N}_4\text{-SiO}_2$ was formed thereover to a thickness of 700 Angstroms. A blue interference colour was obtained over the entire area of the coated surface of the plate.

EXAMPLE 2-2

In the same manner as above, a chromium primer layer was produced with a constant thickness of 500 Angstroms, while the thickness of a light permeable coating layer of $\text{Si}_3\text{N}_4\text{-SiO}_2$ was changed by varying the sputtering time. Interference colours were obtained over the entire area of the coated surface of the plate, that is, yellow interference colour at 1400 Angstroms, red interference colour at 1800 Angstroms, blue purple interference colour at 2000 Angstroms and green interference colour at 2300 Angstroms thickness of the light permeable coating layer respectively. When the thickness of the light permeable coating layer was further increased, an orange interference colour was obtained at a thickness of 2800 Angstroms, but no interference was exhibited if the thickness was increased further.

As has been described above, various interference colours can be obtained depending on the thickness of the light permeable coating layer of $\text{Si}_3\text{N}_4\text{-SiO}_2$. In

this case, the thickness of the light permeable coating layer and the selectivity of the wavelength region were varied with the ingredient ratio of SiO_2 in the composite material showing a tendency that the change of the wavelength region, that is the change in the interference colour with thickness of the light permeable coating layer was moderated with increase in SiO_2 content and that the brightness of the interference was reduced.

10 In view of the relationship with the brightness, the upper limit of SiO_2 was 80% by weight and the maximum thickness of the light permeable coating layer showing an interference colour, which was blue, was 4000 Angstroms.

15 **EXAMPLE 2-3**

When the light permeable coating layer was composed solely of Si_3N_4 , the change of the wavelength region relative to the thickness became sharp, which was unfavourable since it was difficult to obtain an identical interference colour over the entire area of the coated surface in relation to the distribution of the thickness of the light permeable coating layer upon its formation and there was also a problem with reproducibility. Thus it was found preferable that at least 5% by weight of SiO_2 was included in the composite

material. In this case, a clear blue interference colour was exhibited with a thickness of the light permeable coating layer greater than 400 Angstroms and the interference colour changed as described above with
5 increase in the thickness.

Clear yellow and blue interference colours were obtained by the light permeable coating layer of Si_3N_4 - SiO_2 in the intermediate wavelength region.

Although this example has used sputtering it is
10 also possible to use vacuum vapour deposition or ion plating in place of sputtering to achieve a similar effect.

In the case of employing an electron beam as an evaporation source both for vacuum deposition and ion
15 plating, a mirror-finished flat metal plate was placed in a device, Si_3N_4 - SiO_2 composite material with an appropriate ingredient ratio was placed in a crucible and vapour deposition or ion plating was conducted under appropriate evaporating conditions to form a
20 light permeable coating layer on the flat metal plate.

In the case of a flat plate made of resin material, two electron guns and crucibles were disposed in a single device. Metal such as chromium for a primer layer was placed in one crucible and Si_3N_4 - SiO_2
25 composite material with an appropriate ingredient ratio

was placed in the other crucible. The metal was first evaporated by an electron gun to form a primer layer on the flat resin plate and, thereafter, $\text{Si}_3\text{N}_4\text{-SiO}_2$ composite material was evaporated to form a light permeable coating layer.

EXAMPLE 3

In this example, multiple interference colours were obtained simultaneously by considering or controlling the configuration of a light permeable coating layer producing interference colours as described above.

The surface configuration of a watch case frame shown in Figure 2 was designed such that a step was formed to provide a slight difference in parallel distances when viewed in the direction of the arrows and SiC-SiO_2 composite material was sputtered in the direction of the arrows at a sputtering rate of 170 Angstroms/min for about 12 minutes to form a light permeable coating layer.

This produced a difference in the thickness in the light permeable coating layer between a portion nearer to the sputtering source and a portion somewhat more remote therefrom and, as a result, clear interference colours were shown, i.e. green colour at the portion 10A and from pink to red purple at the

portion 10B.

It is of course possible for three, four or more colours to be exhibited utilising slight differences in the thickness of the light permeable coating layer
5 depending on location by making the configuration more complicated.

In this way, it is possible to produce a plurality of tones in one step and a plurality of geometrical tones can be arranged by applying a three-dimensional
10 design to the surface or the cross-sectional configuration.

EXAMPLE 4

When sputtering was applied under the same conditions as in Example 3 for about 10 minutes to a
15 curved portion of a watch case frame 20 shown in Figure 3, interference colours were produced, i.e., a purple blue colour at a central portion 20A and a yellow colour at portions 20B and 20C. That is there was produced a clear tone in which blue colour was sandwiched between
20 yellow colour in a coaxial manner. In the case of the configuration of this watch case frame, the tone was varied continuously.

EXAMPLE 5

In this case, a light permeable coating layer was
25 formed on a watch case 30 comprising a watch case frame

31 and a transparent cover 32 such as a front glass as shown in Figures 4A and 4B.

Plating was applied at first to a member 31A made of ABS resin as the frame 31. Specifically, as shown in
5 Figure 4C, after applying electroless nickel plating 31B to provide a primer layer with a thickness of 0.05 micron, plating was conducted successively, i.e., electrolytic copper plating 31C of 10 microns, electrolytic nickel plating 31D of 10 microns and
10 electrolytic chromium plating 31E of 0.25 microns. After the completion of the plating, the transparent cover 32, made of acrylic resin, was bonded to the frame 31. After the bonding, the watch case 30 was placed in a sputtering device and after reducing the pressure to a
15 vacuum of about $(1.0-2.0) \times 10^{-3}$ Pa, argon gas was injected to a pressure of 6.0×10^{-1} Pa, and $\text{Si}_3\text{N}_4\text{-SiO}_2$ composite material (nitride and oxide of the group IVb element Si) was used as a sputtering target. The SiO_2 ingredient ratio was set to 20% by weight. Sputtering
20 was effected at a high frequency output of 8 Watts/cm² for 7 minutes. As a result a light permeable coating layer 31F composed of $\text{Si}_3\text{N}_4\text{-SiO}_2$ was formed to a thickness of 0.14 micron on the surface of the frame 31. A clear yellow interference colour of transparent
25 feeling was produced on the frame 31 made of ABS resin

formed with the primer layer. On the other hand, as shown in Figure 4D, a $\text{Si}_3\text{N}_4\text{-SiO}_2$ layer 32A was formed on the transparent cover 32 to a thickness of 0.14 micron, which showed an inherent semi-transparent pale brown colour.

In this way, a clear yellow interference colour of transparent feeling and a semi-transparent pale brown colour were well matched with each other and a watch case of high quality feeling was obtained in one sputtering step.

Thus, with the watch case 30, a semi-transparent pale brown colour could be obtained for the transparent cover 32 over a dial plate (not shown) to form a so-called smoked state, which was well matched with the yellow interference colour of the frame 31 thereby obtaining a watch exterior case of high quality feeling.

EXAMPLE 5-2

When sputtering was applied in the same manner as above for a target of $\text{Si}_3\text{N}_4\text{-SiO}_2$ composite material at a high frequency output of 8 Watts/cm² for 3.5 minutes, a light permeable coating layer of $\text{Si}_3\text{N}_4\text{-SiO}_2$ with a thickness of 0.07 micron was produced. The frame 31 exhibited a clear blue interference colour of transparent feeling, whereas the transparent cover 32 exhibited a semi-transparent pale brown colour inherent

to the layer. In this way, it was possible to vary the interference colour of the frame 31 by varying the thickness of the light permeable coating layer.

5 **EXAMPLE 5-3**

When sputtering was applied in the same manner as above by using SiC-SiO_2 composite material (the carbide and oxide of the group IVb element Si) at a high frequency output of 8 Watts/cm² for 8 minutes, a light permeable coating layer of SiC-SiO_2 to a thickness of 0.14 micron was produced and the frame 31 exhibited a clear red interference colour of transparent feeling, whereas the transparent cover 32 exhibited a semi-transparent pale red-brown colour inherent to the layer.

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the transparent cover 32 exhibited the inherent semi-transparent colour of the composite material.

In Examples 5-1 to 5-³/₄, interference colour and semi-transparent colour inherent of the composite material were used together, for example, in a watch case. Referring to the interference colour, clear tone of transparent feeling such as of red, orange, yellow, green, blue, purple blue and purple could be selectively obtained by varying the composition of the composite material and thickness of the light permeable coating layer. The interference colour was well matched with the transparent colour resulting in a frame of high quality feeling. Further, the light permeable coating layers 31F, 32A were generally hard, excellent in abrasion resistance, as well as excellent in corrosion resistance due to their chemical stability. Particularly, in the case of articles of plastics, since the light permeable coating layer functions also as a protective layer, excellent abrasion resistance can be obtained.

In the case where the article is made of metal, the light permeable coating layer can be formed without applying plating to the surface of the article.

C L A I M S

- 5 1. A coloured article comprising a light permeable coating layer made of a mixture consisting of SiC and SiO₂ with a thickness of 200 to 3000 Å, the SiO₂ being present in an amount of 5 to 80% by weight, the coating layer being formed on a reflection surface of a pre-
- 10 determined reflectance.
2. A coloured article comprising a light permeable coating layer made of a mixture consisting of Si₃N₄ and SiO₂ with a thickness of 200 to 4000 Å, the SiO₂ being present in an amount of 5 to 80% by weight, the coating
- 15 layer being formed on a reflection surface of a pre-determined reflectance.
3. A coloured article as claimed in claim 1 or 2 in which the coating layer is formed by vapour deposition, sputtering or ion plating.
- 20 4. A coloured article as claimed in any preceding claim in which the reflection surface comprises a plurality of surfaces different from each other in their distance from or angle relative to the frontmost surface of the article.
- 25 5. A coloured article as claimed in any preceding claim in which the article is of non-metallic material such as synthetic resin or ceramic and the reflection
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surface is a primer layer.

6. A coloured article as claimed in any of claims 1 to 4 in which the article is of metal and the reflection surface is formed by surface treatment.

7. A coloured article as claimed in any preceding claim in which the reflection surface is formed as a curved surface.

8. A coloured article substantially as herein described with reference to and as shown in the accompanying drawings.



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