(54) METHOD OF MAKING LIGHT-ABSORBING COATINGS

(71) We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED of Abacus House, 33 Gutter Lane, London, EC2V 8AH, a British Company, do hereby
5 declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:
10 The invention relates to a method of making light-absorbing coatings having a high absorption in the visible spectrum, and to a substrate bearing a coating made by such a method.
15 Black coatings are used for widely differing purposes. When colouring metals black, the intention is, besides purely aesthetic purposes, to obtain special effects, for example the utilization of optical and
20 heat properties of the black colour, such as the reduction or prevent of the reflection in certain wavelength-ranges of the spectrum. Coatings having the properties of a substantially ideal black body in the waverange
25 of the solar spectrum, which also substantially completely absorb sunlight, however, have a low emission for infra-red radiation above 2.5 μm. They can be used as selective absorbers or, put differently, as selec-
30 tive solar collectors.
In principle there are three possible methods of blackening a metal surface:
A black coating can be deposited on the metal surface, such coatings consist as a
35 rule of a pigment suspension in a binder. Whilst supplying a sufficient covering, such coatings have a relatively high emission value for thermal radiation and, consequently, are not suitable for use as a
40 selective absorber.
Oxide or sulphide layers can be grown by means of a chemical reaction with or on the base metal.
A third possibility is the electrolytic
45 deposition of very finely distributed metals or metal compounds onto the base metal. Coatings of this kind are suitable for use as selective absorbing layers. In the manufacture of this kind of coating, the cathodic reduction of thiocyanate ions in nickel-zinc- 50 salt solutions is known. This method is used for " black nickel-plating " in which nickel and zinc are precipitated as a mixed sulphide on the cathode. " Black chromium-plating " is an electrolytic process in which 55 a low-valency chromium oxide is precipitated from a chromium acid-containing bath (cf. " Oberfläche-Surface ", *11* (1970), 12, pages 302 etc.).
The absorption properties of electro- 60 deposited coatings may be based on the fact that only the material properties of the deposits become active, but structural properties of the deposit (for example a pronounced erosion of the surface) may in- 65 crease the absorption. The properties of these coatings which are in most cases very thin are, however, not only affected by their structure and the type of chemical compounds which participate in their build-up, 70 but also by the surfaces and the structure of the base material on which they are deposited.
If coatings of this type are used as selective absorbers for sunlight, they are only 75 usable within a narrow range of layer thicknesses. The coating must be just so thick that the highest possible absorption is obtained in the visible spectrum, whereas for the characteristic radiation of the 80 absorption arrangement, the radiation properties of the metal substrate must, if possible, be maintained. So the thickness of the coating must be small compared with the maximum wavelength of infra-red radia- 85 tion at the operating temperature. For an operating temperature of 100°C, this wavelength is approximately 10μm. Only under these conditions is it possible to keep the emissitivity for infra-red radiation of the 90

metal plus coating at a minimum. With thicker coatings the considerably higher emission values of the compact coating material are quickly obtained so that there is no longer question of selective absorption.

The known black nickel coatings are not suitable for use as selective absorbers as they have an unsatisfactory long-term stability at higher temperature, particularly in vacuum. In addition, when only one absorption coating is deposited it is hardly possible to obtain values higher than 0.9 for the absorption in the visible spectrum and an emission of infra-red radiation of approximately 0.1.

The invention provides a method of producing a light-absorbing coating comprising cobalt sulphide on an infra-red reflecting-metal layer, said coating having an absorption of more than 0.9 in the visible spectrum and an emission of 0.1 or less for infra-red radiation, the method comprising the step of electrodepositing a coating onto the infra-red-reflecting metal layer from an aqueous electrolyte which contains an alkali metal thiocyanate and a water-soluble cobalt compound, with/without a water soluble nickel compound and/or a water-soluble iron compound, wherein the ratio of the weight of the alkali metal thiocyanate to the total weight of the water-soluble cobalt compound, water-soluble nickel compound and water-soluble iron compound in the electrolyte is in the range from 2:1 to 1:20. The said weight ratio is preferably in the range from 1:1 to 1:5. Preferably the infra-red-reflecting metal layer consists of silver.

The invention is based on the recognition that in sulphide systems cations are substitutable over large concentration ranges. Metastable sulphide phases can be stabilized by mixed crystal formation and lattice defects can be compensated for.

The advantages obtained with the invention particularly consist in that a coating cobalt sulphide can be formed in a technologically very simple manner, which coating has a substantially total absorption in the visible spectrum but only a low emissitivity for infra-red radiation, it being possible to adjust the required thickness of the coating accurately to a defined value without difficulty by means of a corresponding adjustment of the current density and the duration of the electrolytic process. Surprisingly, the optimum thickness of the coating can be adjusted with given starting electrolytes by means of a subsequent chemical etching operation with mineral acids, which is in contradiction with the experience in analytical chemistry, where CoS and NiS remain insoluble in the chemical separation process under similar conditions. On the other hand, it is surprising and unexpected that the values for the absorption in the visible spectrum increase during etching, as normally the absorption in the visible spectrum increases with increasing thickness of the coating.

The method according to the invention may be used to deposit a light-absorbing coating on an intermediate layer or on the outside of a stack of intermediate layers of infra-red reflecting metal on an electrically non-conducting substrate.

Some embodiments of the invention will now be described with reference to the following Examples and to the accompanying drawing, the single Figure of which shows the dependence of the value for the absorption α_s in the and for the emission ε of infra-red radiation at given operating conditions for an absorber having a CoS-coating made as described in Example I.

Example I.

Selectively absorbing cobalt sulphide coatings can be produced from electrolytes whose salt content may vary within wide limits. Both the chloride and also other cobalt salts, for example sulphate, nitrate or acetate can be utilized.

A typical composition of the electrolyte contains 2.5% by weight $CoCl_2.6H_2O$ and 2.5% by weight KSCN. Favourable current densities are between 0.1 and $1A/dm^2$. At $0.5A/dm$ and a period of electrolysis of approximately 1 minute, copper and nickel sheets can be coated so that the following values for the absorption α_s in the visible spectrum and for the emission $\varepsilon_{90}{}^\circ c$ of infra-red radiation at an operating temperature of the absorber of 90°C can be obtained in a reproducible manner. $\alpha_s = 0.97$ and $\varepsilon_{90}{}^\circ c := 0.06\text{-}0.07$ on copper substrates, $\alpha_s = 0.97$ and $\varepsilon_{90}{}^\circ c = 0.07\text{-}0.08$ on nickel substrates and $\alpha_s = 0.96$ and $\varepsilon_{90}{}^\circ c = 0.04$ on silver-plated glass substrates.

The drawing shows values for the absorption α_s in the visible spectrum and for the emission $\varepsilon_{90}{}^\circ c$ of infra-red radiation at an operating temperature T=90°C of an absorber having cobalt sulphide layers prepared using different current densities (A/dm^2) and periods of electrolysis (t expressed in seconds) and the anode material, the electrolyte being used at room temperature. The coatings are then less than $0.1\mu m$ thick. The measuring points are differentiated according to the current densities used as indicated, with an Ni anode for the first-mentioned value of current density and an Al anode for the remaining values.

Example II.

A selectively light-absorbing mixed cobalt-nickel sulphide coating is cathodically deposited from an electrolyte. having one of the following compositions:

2.5 g $CoCl_2.6H_2O + 2.5$ g $NiCl_2.6H_2O + 5$ g KSCN in 200 ml H_2O

or

5.0 g $CoCl_2.6H_2O + 1.0$ g $NiSO_4.6H_2O + 5$ g KSCN in 200 ml H_2O

or

5.0 g $CoCl_2.6H_2O + 1.0$ g $Ni(NO_3)_2.6H_2O + 5$ g KSCN in 200 ml H_2O,

under comparable conditions as described in Example I.

The following values are obtained for the absorption α_s in the visible spectrum and for the emission $\varepsilon_{90}°_c$ of infra-red radiation $\varepsilon : \alpha_s = 0.96$ and $\varepsilon_{90}°_c = 0.08$.

Example III.

A selectively light-absorbing mixed cobalt-nickel sulphide coating is deposited from an electrolyte having the following composition:

10% by weight $NiCl_2.6H_2O$, 7% by weight $CoCl_2.6H_2O$, 2.5% by weight KSCN and 4% by weight NH_4Cl in water.

The procedure is such that in a first step after an electrolysis period of approximately 1 to 2 minutes at a current density of 0.5 A/dm^2 at room temperature, a coating is obtained having a value of α_s of approximately 0.6 and which layer has a bright metallic appearance. In a second step this coating is then etched for approximately 0.5 minutes with 2N HCl to a thickness which yields a value of α_s of 0.93 and a value of $\varepsilon_{90}°_c$ of 0.07.

The fact that the value for α_s is higher in this Example after etching can presumably be traced back to the influence of ammonium ions in the formation of the layer.

Example IV.

If cobalt sulphide is deposited on iron in accordance with the conditions described in Example I, then a value of α_s of 0.93 and a value of $\varepsilon_{90}°_c$ of 0.10 can be obtained. However, the deposit is not so homogeneous as on copper or nickel. This is presumably caused by the cubic body-centered structure of iron, whose lattice constant is approximately 20% smaller than that of copper and nickel. Copper and nickel have cubic face-centered lattices, whose lattice constants corresponds to within a few percent to the *a*-axis of the sulphide which crystallizes with a B8-type structure. For an improved "chemical matching" 0.25% by weight $FeCl_2.4H_2O$ or 0.25% by weight $FeSo_4.7H_2O$ or 0.25% by weight $Fe(NO_3)_3.9H_2O$ is added to the electrolyte which has a composition of 2.5% by weight $CoCl_2.6H_2O$ + 2.5% by weight KSCN. At a current density of 0.5A/dm^2 and a dura-

tion of electrolysis of approximately 1 minute, the following values are obtained $\alpha_s = 0.98$ and $\varepsilon_{90}°_c = 0.08$.

The same values are obtained with this electrolyte on iron and nickel substrates. When copper is used as a substrate, the same value of α_s (0.98) is obtained but $\varepsilon_{90}°_c$ is only 0.05.

In the Co-Fe-sulphide system the most favourable combinations for the values for α_s and $\varepsilon_{90}°_c$ are at a high ratio of cobalt to iron. If this ratio becomes very small then an etching operation is necessary as described in Example III. Then it is possible to obtain the following values: for $\alpha_s = 0.94$ and for $\varepsilon_{90}°_c = 0.1$.

WHAT WE CLAIM IS:—

1. A method of producing a light-absorbing coating comprising cobalt sulphide on an infra-red reflecting metal layer, said coating having an absorption of more than 0.9 in the visible spectrum and an emission of 0.1 or less for infra-red radiation, the method comprising the step of electrodepositing a coating onto the infra-red reflecting metal layer from an aqueous electrolyte which contains an alkali metal thiocyanate and a water-soluble cobalt compound, with/without a water-soluble nickel compound and/or a water-soluble iron compound, wherein the ratio of the weight of alkali metal thiocyanate to the total weight of the water-soluble cobalt compound, water-soluble nickel compound and water-soluble iron compound in the electrolyte is in the range from 2:1 to 1.20.

2. A method as claimed in Claim 1, wherein the ratio of the weight of the alkali metal thiocyanate to the total weight of the water-soluble cobalt compound, water-soluble nickel compound and water-soluble iron compound is in the range from 1:1 to 1:5.

3. A method as claimed in Claim 1 or Claim 2, wherein the infra-red reflecting metal layer consists of silver.

4. A method as claimed in any preceding Claim, wherein the thickness of the electrodeposited coating is adjusted by etching with a mineral acid.

5. A method of producing a light-absorbing coating comprising cobalt sulphide of an infra-red-reflecting metal layer, said coating having an absorption of more than 0.9 in the visible spectrum and an emission of 0.1 or less for infra-red radiation, substantially as herein described with reference to any of Examples I to IV.

6. An assembly comprising a light-absorbing coating produced by a method

as claimed in any preceding Claim on an infra-red-reflecting layer.

7. An electrically non-conducting substrate bearing an intermediate layer or a
5 plurality of intermediate layers of infra-red-reflecting metal and a light-absorbing coating deposited on an intermediate layer or on the outside of a stack of intermediate layers by the method as claimed in any of Claims 1 to 5. 10

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α_s, ϵ

α_s

ϵ 90°C

t (sec)

• 0,8 A/dm²
+ 0,8 A/dm²
x 0,5 A/dm²
▲ 0,3 A/dm²