

(19)



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European Patent Office
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(11)

EP 0 721 084 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.08.2001 Bulletin 2001/33

(51) Int Cl.7: **F21V 7/22**

(21) Application number: **95120298.5**

(22) Date of filing: **21.12.1995**

(54) **Method of treatment for reflectors made of metallic material**

Verfahren zur Behandlung von Reflektoren aus Metall

Méthode de traitement de réflecteurs métalliques

(84) Designated Contracting States:
DE ES FR GB

(30) Priority: **29.12.1994 IT TO941093**

(43) Date of publication of application:
10.07.1996 Bulletin 1996/28

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Description

[0001] The present invention relates to a method of treatment for reflectors made of metallic material, for example stamped in ferrous sheet or diecast in aluminium alloy, with the dual aim of ensuring protection of the metallic material of the reflector against corrosion and of providing a reflecting surface with suitable photometric characteristics.

[0002] It is known that the reflectors of vehicle headlights are at present made either by moulding from a synthetic plastic, or by stamping from ferrous plate, or by diecasting of an aluminium alloy (or other light alloy). In the second and third cases, the aforementioned reflectors must at present follow a process of treatment and of painting that is completely different from that adopted for reflectors in plastics, using different treatment lines with consequent increases of costs. On the other hand, application of all or part of the cycle of treatment of reflectors made of plastics to those made of a metallic material would on the one hand lead to extremely poor photometric characteristics being obtained, owing to the fact that the surface roughness of reflectors made of metallic material is much greater than that of reflectors made of plastics and, on the other hand, would lead to serious problems of corrosion, especially in the case of reflectors provided with welded brackets for mounting on the bodywork and/or with accessory elements of the headlight, such corrosion being attributable to the operating conditions, which envisage the formation of possible condensation inside the headlight, with subsequent rapid evaporation as a result of heating when the headlight is switched on.

[0003] The aim of the invention is to provide a method of treatment of reflectors made of metallic material by which it is possible to apply to them at least a large part of the treatment cycle normally employed for reflectors made of synthetic plastics, though without giving rise to the problems described above.

[0004] On the basis of the invention, therefore, a method of treatment is provided for a reflector made of a metallic material, to make the reflector resistant to corrosion and at the same time to provide it with a suitable reflecting surface, the method being **characterized** in that it comprises, in combination, the following stages:

- a pre-treatment of amorphous phosphating;
- application of primer by electrodeposition and subsequent polymerization of the primer at high temperature;
- premetallizing painting with UV-photopolymerizable paints, in the same way as is done on reflectors moulded in synthetic plastics; and
- metallizing under vacuum.

[0005] In particular, the said application of primer is effected by cataphoresis and subsequent baking of the painted reflector at a temperature such as to develop,

on the reflector, a temperature of polymerization of the previously applied primer above 200°C.

[0006] In this way, by means of the stages of pretreatment and priming, there is a considerable decrease in the initial surface roughness of the reflector, in particular on account of the stage of amorphous phosphating (an effect that cannot be obtained with crystalline phosphating as is much more commonly employed, see e.g. document JP-A- 57 164 976) and complete protection of the reflector against corrosion; in particular, it is believed that corrosion due to the operating conditions is hindered by the same mechanism that forms the basis of cataphoretic protection of sheet metal for bodywork, improved by the higher degree of crosslinking of the cataphoretic resin obtained by effecting the stage of polymerization of the resin, after it has been applied, at a much higher temperature (above 200°C) than that used in the usual technology of cataphoresis for elements of bodywork.

[0007] Moreover, execution of cataphoresis at high temperature also has a degassifying effect both on the cataphoresis layer and on the underlying phosphated layer, which obviates the risk of formation of gas bubbles in the paint films during execution of metallizing under vacuum, thus making it possible to adopt the same cycles at high vacuum (10^{-3} or 10^{-4} millibar) used for reflectors made of plastics.

[0008] In conclusion, the new combination of known stages of protection, traditionally employed on sheet metal, but with the variant of execution at high temperature and in the amorphous phase, with stages, though known in themselves, of UV paint treatment and metallizing at high vacuum, that are typical of operations on reflectors made of plastics, surprisingly makes it possible for the same cycle of painting/metallizing used for headlights made of plastics to be adopted for reflectors made of metallic material, even using the same equipment, with consequent substantial economies of scale and rationalization of the production cycles. At the same time, the stages of pretreatment make it possible to reduce the roughness to suitable levels and to obtain good corrosion protection in service, but without detriment to the quality of execution of the subsequent stages. Finally, the cycle of treatment according to the method of the invention leads to an energy saving compared to the known cycles of treatment of reflectors made of metallic material of at least 20% and a more favourable environmental impact.

[0009] Other characteristics and advantages of the invention will become clear from the description that follows.

[0010] Reflectors for vehicle headlights are made in a known way from a metallic material, for example by stamping and trimming of ferrous metal sheet, or by diecasting of an aluminium alloy. These reflectors are then treated according to the invention to make them resistant to corrosion and at the same time to give the said reflectors a reflecting surface with suitable photometric

characteristics. These normally incompatible characteristics are obtained according to the invention by first effecting a pretreatment of phosphating the whole surface of the reflectors.

[0011] However, in contrast to the majority of similar treatments effected on metallic material, the phosphating is executed amorphously, i.e. by depositing a non-crystalline covering layer on the reflector; for example, the amorphous phosphating stage is accomplished by the well-known process of light ferric phosphating, preceded by alkaline degreasing, first by spraying and then by immersion, with intermediate rinses, and followed by washings with demineralized water, the whole according to operating cycles that are well known to persons skilled in the art and which therefore will not be described in detail here.

[0012] Next, a stage of application of primer is effected on the reflectors. This is carried out according to the invention by electrodeposition and subsequent polymerization of the paint at high temperature; "high temperature" is to be understood as meaning a temperature that is appreciably higher than that usually employed in paint treatments by electrodeposition for bodywork sheet. In particular, the priming stage is accomplished by cataphoresis and subsequent baking of the painted reflector at a temperature such as to develop on the reflector (i.e. to raise the workpiece temperature physically) to a temperature of polymerization of the previously applied primer above 200°C.

[0013] The stage of deposition of the paint by cataphoresis is effected by immersion, according to operating cycles that are well known and therefore, for simplicity, will not be described in detail here. It will suffice to specify here that during this stage of application of primer a paint film with thickness between 18 and 24 µm, and preferably equal to 20 µm, is electrodeposited, the paint used being a mixture of known anticorrosion pigments and at least one water-compatible epoxy resin possessing isocyanate groups. According to one of the fundamental characteristics of the invention, after deposition of the paint by cataphoresis and several rinses with ultrafiltrate and demineralized water, a stage of hot polymerization or "baking" of the paint is effected, maintaining a workpiece temperature of about 220°C for 20-30 minutes.

[0014] From this point on, the pretreated and primer-coated reflectors are submitted, according to the invention, to the same cycle of treatment and painting as is known for reflectors made of plastics, using for this purpose the same equipment that was developed and is used for reflectors made of plastics. In particular, a stage of premetallizing painting is effected first, applying a film of UV-photopolymerizable paint to the reflector surfaces, in the same way as is done on reflectors moulded in synthetic plastics and to a thickness between 27 and 35 µm and preferably equal to 30 µm; this stage is executed by first effecting an activation pretreatment by bombarding the reflectors with UV rays, then applying the paint,

preferably by immersing the reflectors in a liquid bath (or alternatively by spraying or by "flow-coating") followed by draining and a resting stage during which the paint is submitted to IR irradiation, causing its desolvation (elimination of the solvent) and flow or levelling. Finally, the painted reflectors are submitted to a stage of photopolymerization of the paint, bombarding them with UV rays, and they are then baked in an air-circulating stove at a temperature of about 180°C.

[0015] The reflectors are then cooled and are submitted to a metallizing stage, also known, which consists of coating the painted reflector with a film of aluminium by ion discharge and subsequent evaporation at high vacuum (effected at 10⁻⁴ millibar) or by sputtering at a reduced pressure of about 10⁻³ mbar. In both cases, the said stage of metallizing is followed by a stage of deposition of a protective film on the metallized film.

[0016] According to a first possibility, the protection stage can consist of protective painting, by coating the aluminium film with a layer of a transparent lacquer of any known type that is suitable for the purpose, with thickness between 5 and 10 µm, and which is heat-polymerizable. Alternatively, the protection stage can consist of the direct deposition, on the aluminium film, of a protective film of monomers, which are then polymerized directly on the film itself by the cold-plasma, low-vacuum polymerization system, according to a technique that is well known in the field of vacuum treatment of plastics reflectors.

[0017] The invention will now be further described, referring to the following example of practical embodiment.

EXAMPLE

[0018] A batch of reflectors made of stamped and semitrimmed steel sheet, of various shapes and dimensions, some of which are provided with brackets or other accessories fixed directly to the reflector by welding, is submitted to the following processing:

- a stage of preliminary spray degreasing, followed by a stage of degreasing by immersion in a suitable bath; the products CLEANSTONE L160HP™ and CLEANSTONE SD145™ respectively, from the company ITB, are used, adhering strictly to the manufacturer's instructions given in the data sheet supplied with the product;
- a stage of amorphous phosphating, effected with the product DEPHOS ML439™ from the company ITB, following the manufacturer's instructions;
- a stage of deposition of a coat of primer (thickness from 18 to 24 µm) effected by cataphoresis using immersion equipment, maintaining a direct-current (DC) voltage of 200-250 V between the electrodes, using the products CATHODIP GY830260™ (binder) and CATHODIP GV849436™ (paste) from the company BASF, following the manufacturer's in-

structions;

- a stage of baking in an air-circulating stove for 25 minutes at 220°C measured on the workpieces;
- a stage of premetallizing painting, which is effected by depositing films of between 27 and 35 µm of single-component paint HQ793825™ from BASF company by immersion, after irradiating the reflectors with UV at a wavelength of 350-385 nm, with subsequent desolvation and levelling obtained by IR irradiation for 150 seconds and photopolymerization of the paint by UV irradiation effected with a PHILIPS high-pressure Hg lamp, finishing by stoving at 180°C for 35 minutes;
- a stage of deposition of a film of Al at high vacuum (10⁻⁴ mbar) preceded by ion discharge at low vacuum (10⁻² mbar);
- a stage of protection by deposition, on the Al film, of a layer or film of lacquer VE359™ from the company COVECO, applied according to the manufacturer's instructions.

[0019] At the end of the production process, all the reflectors exhibited a highly reflective surface and excellent surface finish, with a low degree of roughness. When submitted to accelerated ageing testing according to the requirements of the procurement specifications of the world's principal car makers, all the reflectors passed the tests exceptionally well, with better results than similar reflectors that had undergone conventional processes.

Claims

1. Method of treatment for a reflector made of a metallic material, to make the reflector resistant to corrosion and at the same time to provide it with a suitable reflecting surface, the method being **characterized** in that it comprises, in combination, the following stages:
 - a pretreatment of amorphous phosphating;
 - application of primer by electrodeposition and subsequent polymerization of the primer at high temperature;
 - premetallizing painting with UV-photopolymerizable paints, in the same way as is done on reflectors moulded in synthetic plastics; and
 - metallizing under vacuum.
2. Method according to Claim 1, characterized in that the said application of primer is effected by cathoresis and subsequent baking of the painted reflector at a temperature such as to develop, on the reflector, a temperature of polymerization of the previously applied primer above 200°C.
3. Method according to Claim 2, characterized in that

in the said stage of application of primer, a paint film with thickness between 18 and 24 µm is electrodeposited; the said stage of baking at a workpiece temperature above 200°C being continued for 20-30 minutes.

4. Method according to Claim 2 or 3, characterized in that the paint used is a mixture of anti-corrosion pigments and a water-compatible epoxy resin possessing isocyno groups.
5. Method according to one of the preceding claims, characterized in that the said stage of amorphous phosphating is accomplished by light ferric phosphating preceded by alkaline degreasing, first by spraying and then by immersion, and followed by washings with demineralized water.
6. Method according to one of the preceding claims, characterized in that the stage of premetallizing painting is effected with the same equipment for executing an analogous premetallizing painting on reflectors made of synthetic plastics and consists of depositing a photopolymerizable resin on the reflector to a thickness between 27 and 35 µm, preceded by a pretreatment of UV-radiation activation of the primer-coated reflector and followed by a treatment with IR radiation, UV photopolymerization and post-stoving.
7. Method according to Claim 6, characterized in that the said post-stoving is executed in an air-circulating stove, at a temperature of at least 180°C.
8. Method according to one of the preceding claims, characterized in that the said stage of vacuum metallizing consists of coating the painted reflector with a film of Al by ion discharge and subsequent evaporation at high vacuum (10⁻⁴ mbar) or by sputtering at a reduced pressure of about 10⁻³ mbar.
9. Method according to Claim 8, characterized in that the said stage of metallizing is followed by a stage of deposition of a protective film.
10. Method according to Claim 9, characterized in that the protection stage consists of protective painting, by coating the aluminium film with a layer of a transparent lacquer with thickness between 5 and 10 µm that is heat-polymerizable.
11. Method according to Claim 9, characterized in that the protection stage consists of direct deposition under vacuum, on the aluminium film, of a film of monomers, which are polymerized directly on the Al film by cold-plasma polymerization.

Patentansprüche

1. Verfahren zur Behandlung eines aus einem metallischen Werkstoff hergestellten Reflektors, um den Reflektor gegen Korrosion widerstandsfähig zu machen und um ihn gleichzeitig mit einer geeigneten reflektierenden Oberfläche zu versehen, wobei das Verfahren dadurch gekennzeichnet ist, daß es in Kombination die folgenden Schritte enthält:

- Vorbehandlung der amorphen Phosphatierung;
- Aufbringung einer Grundierung durch Elektroablagerung und nachfolgende Polymerisation der Grundierung bei hoher Temperatur;
- vormetallisierender Anstrichauftrag mit UV-polymerisierbaren Anstrichmitteln in der gleichen Weise wie dies an Reflektoren erfolgt, die aus Kunststoffen gegossen sind; und
- Metallbedampfung bei Unterdruck.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Aufbringung der Grundierung durch Kataphorese und nachfolgendes Brennen des farbbeschichteten Reflektors bei einer Temperatur, bei der sich auf dem Reflektor eine Polymerisationstemperatur der zuvor aufgetragenen Grundierung oberhalb 200 °C entwickelt, erfolgt.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß im Schritt der Aufbringung der Grundierung ein Anstrichfilm mit einer Dicke zwischen 18 und 24 µm durch Elektroablagerung aufgebracht wird; wobei der Schritt des Brennens bei einer Werkstücktemperatur oberhalb 200 °C während 20 bis 30 Minuten andauert.

4. Verfahren nach Anspruch 2 oder 3, dadurch gekennzeichnet, daß der verwendete Anstrich eine Mischung aus Antikorrosionspigmenten und wasserkompatiblen Kunstharz, das Isozyano-Gruppen besitzt, ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Schritt der amorphen Phosphatierung durch Licht-Ferriphosphatierung ausgeführt wird, der eine alkalische Entfettung zuerst durch Sprühen und anschließend durch Tauchen vorhergeht, und der Waschvorgänge mit entmineralisiertem Wasser folgen.

6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Schritt des vormetallisierenden Anstrichauftrags mit der gleichen Ausrüstung erfolgt, die zur Ausführung eines analogen vormetallisierenden Anstrichauftrags an aus Kunststoffen hergestellten Reflektoren dient, und die Ablagerung eines photopolymerisierbaren

Harzes auf dem Reflektor bis zu einer Dicke zwischen 27 und 35 µm enthält, wobei dieser eine Vorbehandlung der UV-Strahlungsaktivierung des mit Grundierung beschichteten Reflektors vorangeht und eine Behandlung mit IR-Bestrahlung, UV-Photopolymerisation und Nachbrennen folgt.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Nachbrennen in einem Ofen mit Luftzirkulation bei einer Temperatur von wenigstens 180 °C ausgeführt wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Schritt der Unterdruck-Metallbedampfung das Beschichten des mit Anstrichauftrag versehenen Reflektors mit einem Aluminiumfilm durch Ionenentladung und nachfolgendes Aufdampfen bei hohem Unterdruck (10⁻⁴ mbar) oder durch Sputtern bei einem verminderten Druck von etwa 10⁻³ mbar enthält.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß dem Schritt der Metallbedampfung ein Schritt der Ablagerung eines Schutzfilms folgt.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß der Schutzschritt einen schützenden Farbauftrag durch Beschichten des Aluminiumfilms mit einer Schicht aus einem photopolymerisierbaren durchsichtigen Lack mit einer Dicke zwischen 5 und 10 µm enthält.

11. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß der Schutzschritt die Direktablagerung bei Unterdruck auf dem Aluminiumfilm eines Films aus Monomeren, die direkt auf dem Aluminiumfilm durch Kaltplasma-Polymerisation polymerisierbar sind, umfaßt.

Revendications

1. Procédé de traitement concernant un réflecteur constitué d'une matière métallique, pour rendre le réflecteur résistant à la corrosion et, en même temps, pour le doter d'une surface réfléchissante appropriée, le procédé étant caractérisé en ce qu'il comprend, de façon combinée, les étapes suivantes :

- un prétraitement de phosphatation amorphe ;
- l'application d'une peinture primaire par électrodéposition, puis la polymérisation de la peinture primaire à haute température ;
- la prémétallisation de la peinture en utilisant des peintures photopolymérisables par rayonnement ultraviolet, de la même manière que celle utilisée sur des réflecteurs moulés dans

- des matières plastiques synthétiques ; et
- la métallisation sous vide.

2. Procédé selon la revendication 1, caractérisé en ce que ladite application de la peinture primaire est effectuée par cataphorèse puis par cuisson du réflecteur peint, à une température telle qu'elle permet d'atteindre, sur le réflecteur, une température de polymérisation de la peinture primaire appliquée précédemment, supérieure à 200°C. 5
3. Procédé selon la revendication 2, caractérisé en ce que au cours de ladite étape d'application de la peinture primaire, un film de peinture ayant une épaisseur comprise entre 18 µm et 24 µm est électrodéposé ; ladite étape de cuisson à une température de pièce d'usinage supérieure à 200°C étant poursuivie sur une période de 20 à 30 minutes. 10 15
4. Procédé selon la revendication 2 ou 3, caractérisé en ce que la peinture utilisée est un mélange de pigments anticorrosion et d'une résine époxyde compatible avec l'eau, ayant des groupes isocyno. 20
5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ladite étape de phosphatation amorphe est réalisée par une phosphatation ferrique légère précédée d'un dégraissage alcalin, en premier lieu par pulvérisation puis par immersion, enfin par des lavages avec de l'eau déminéralisée. 25 30
6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'étape de pré-métallisation de la peinture est effectuée avec le même équipement permettant de réaliser une pré-métallisation de la peinture analogue à celle effectuée sur des réflecteurs en matière plastique synthétique, cette étape de peinture consistant à déposer une résine photopolymérisable sur le réflecteur, cette résine ayant une épaisseur comprise entre 27 µm et 35 µm, cette étant précédée d'un prétraitement d'activation par rayonnement ultraviolet du réflecteur recouvert de la peinture primaire, cette étape étant suivie d'un traitement par rayonnement infrarouge, d'une photopolymérisation par rayonnement ultraviolet et d'un post-traitement dans une étuve. 35 40 45 50
7. Procédé selon la revendication 6, caractérisé en ce que ledit post-traitement dans une étuve est exécuté dans une étuve à circulation d'air, à une température au moins de 180°C. 55
8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ladite étape de métallisation sous vide comprend l'application, sur

le réflecteur peint, d'un film d'aluminium (Al) par décharge d'ions, puis l'évaporation sous vide poussé (10^{-4} mbar) ou la pulvérisation cathodique à une pression réduite environ de 10^{-3} mbar.

9. Procédé selon la revendication 8, caractérisé en ce que ladite étape de métallisation est suivie d'une étape de dépôt d'un film de protection.
10. Procédé selon la revendication 9, caractérisé en ce que l'étape de protection comprend une peinture de protection, en appliquant, sur le film d'aluminium, une couche de laque transparente et thermopolymérisable ayant une épaisseur comprise entre 5 µm et 10 µm.
11. Procédé selon la revendication 9, caractérisé en ce que l'étape de protection se compose d'un dépôt direct sous vide, sur le film d'aluminium, d'un film de monomères qui sont polymérisés directement sur le film d'aluminium (Al) par polymérisation d'un plasma froid.