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- (71) Applicant: DR. HESSE GMBH & CIE. KG [DE/DE];

Werningshof 14, 33719 Bielefeld (DE).
- (72) Inventor: BREMICKER, Tom Nicolai; c/o Dr. Hesse

GmbH & Cie KG, Werningshof 14, 33719 Bielefeld (DE).
- (74) Agent: DOMPATENT VON KREISLER SELTING

WERNER - PARTNERSCHAFT VON PATENTAN-

WÄLTEN UND RECHTSANWÄLTEN MBB; Deich-

mannhaus am Dom, Bahnhofsvorplatz 1, 50667 Köln (DE).
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(54) Title: PROCESS FOR PICKLING NON-CONDUCTIVE PLASTICS

(57) Abstract: What has been surprisingly found with the present process is a stable pickling process for the subsequent plating of plastics, such as acrylonitrile-butadiene-styrene copolymer (ABS copolymer), without using chromium(VI) compounds that can also be integrated into existing plastic plating plants. In addition to ecological advantages, such integration also has economic advantages, since this process can be operated at lower temperatures and thus lower energy cost. In addition, significant advantages in the coating of multicomponent assemblies were surprisingly found, because these could be coated substantially more simply than previously.

Process for Pickling Non-Conductive Plastics

The present invention relates to a process for metallizing non-conductive plastic materials, wherein said pickling is effected without using chromium(VI) compounds. After the pickling, the plastics can be metallized by using known processes.

Articles made of electrically non-conducting plastic can be metallized with an electroless metallizing method, or alternatively with a direct metallizing method. In both methods, the plastic article is cleaned and pickled at first, then mostly treated with a precious metal, and finally metallized. The state of the art is pickling in chromosulfuric acid. The pickling serves to create the base for subsequent metallization. This takes place by the formation of minute cavities, which provide that the surface of the plastic can be wetted, and by which a sufficient adhesion of the deposited metal can be realized.

The components are fixed on frames with frame hooks. Mostly, several components are fixed on one frame. Such frames are coated with a plastic insulation, mostly of poly(vinyl chloride) (PVC). Only the frame hooks, which are mostly made of stainless steel or titanium, are not isolated because they serve for both contacting and attachment of the components.

Usually, for example, plastics such as acrylonitrile-butadiene-styrene copolymer (ABS copolymer) are etched or pickled using the known chromosulfuric acid method in such a way that the microcavities as mentioned above form in sufficient number to ensure a metallic deposition with sufficient adhesion. The chromosulfuric acid, which contains chromium(VI), performs an oxidative attack on the polybutadiene moieties of the polymer. These polybutadiene moieties are removed oxidatively from the polymer surface, so that cavities form at the corresponding positions. In other plastics, the oxidative attack correspondingly takes place at different polymer moieties.

Following this so-called etching or pickling, the plastics to be metallized are activated by means of an electroless activator, which usually contains precious

metals, but mostly either palladium or silver particles, and are thereafter either metallized by electroless plating, which is in the case of direct metallization, or subject to electroless acceleration at first, followed by electroless plating. Thereafter, the components can be directly subjected to electroplating.

The known pickling solutions based on chromosulfuric acid are also used to coat so-called multicomponent plastics. In such multicomponent plastics, several plastics are bonded together in an injection-molding process, or successively injected into the mold. This results in areas that are mostly made of pure PC (polycarbonate), for example, and ABS or an ABS-PC mixture on the other side.

Such components are utilized for preparing, for example, buttons in automobile industry with an optical fiber in the form of some lettering or the like. In this case, for example, the optical fiber is the pure PC (polycarbonate) component, while the other component is a pure ABS or ABS-PC blend that is to be electroplated exclusively.

The known conventional processes based on chromium sulphuric acid pickling only allow a safe, selective coating that only coats the desired areas in combination with a special accelerator or an adapted activation process.

Thus, at least one additional tank with a separate activation process and at least one additional tank with a separate accelerating process (in a conventional procedure) must be respectively present. These are then usually used exclusively for such multicomponent assemblies, because in part different activators and other accelerators or modified parameters are employed here.

Thus, currently, such solutions require more space and exact control and monitoring thereof, in order to ensure a flawless coating.

Since pickling solutions based on chromosulfuric acid are toxic, the use thereof has been strongly restricted in recent years. In addition, it is to be considered that the authorization for the use of chromium trioxide by the ECHA/EU, which is required already now, will not be prolonged indefinitely, and that a ban of use lies ahead.

Therefore, there is a need for a process for pickling non-conductive plastics that is free of toxic compounds, especially free of chromium(VI) compounds. However, the process should be able to provide a comparable adhesion of the subsequently deposited metallic layer on the plastic surface. It should be possible to integrate the pickling process into existing plants without cycle time losses, i.e., without reducing the amount produced per time. In particular, non-conductive plastics are selected from acrylonitrile-butadiene-styrene copolymer (ABS copolymer), polyamide (PA), polycarbonate (PC), mixtures of an ABS copolymer with at least one further polymer, and multicomponent plastics. These should be capable of selective plating after pickling as described above. Surprisingly, it has been found that a process in which a monomer is detached from the plastic surface meets these criteria.

Therefore, in a first embodiment, the object of the present invention is achieved by a process for pickling non-conductive plastic surfaces, wherein said plastic contains polystyrene moieties, characterized by the steps of

- a) providing an article having a surface made of a non-conductive plastic material,
- b) contacting said surface with a pickling solution, wherein said pickling solution contains a solvent and a pickling agent, and
- c) rinsing the surface to remove the pickling agent,

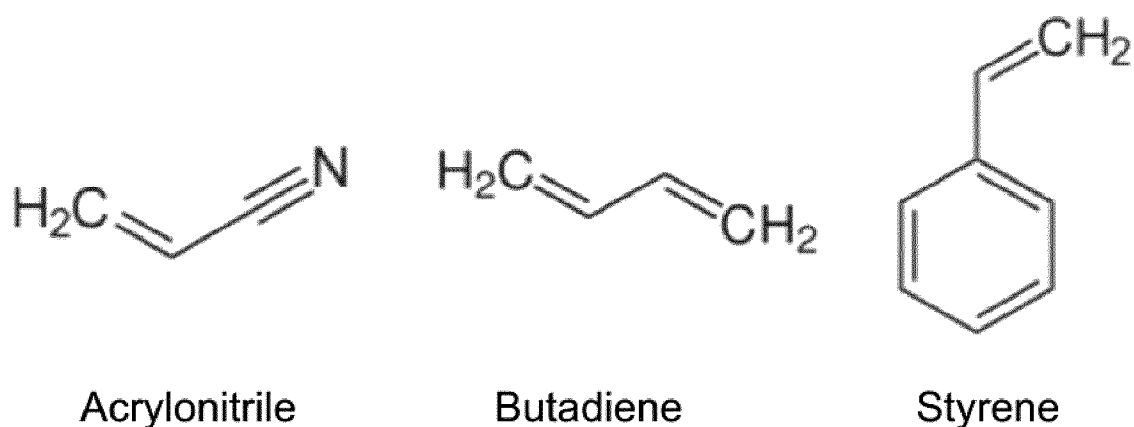
wherein said pickling agent is capable of detaching polystyrene moieties from a polymer.

Surprisingly, it has been found that it is possible to pickle a non-conductive plastic surface for preparing metallization, without having an oxidative attack on the polymer and, in particular, on polybutadiene moieties of a polymer. Rather, it has been found that it is possible to select the pickling agent so that polystyrene moieties are selectively detached. This also creates cavities in the surface, which enable subsequent metallization (plating).

The process according to the invention enables the surface to be changed by pickling. Pickling and etching are both chemical processes that change the surface properties of a material. An etching process involves removal of a material by using an etching agent. In contrast, pickling changes the surface of the material. According to the invention, a pickling agent is employed for pickling a non-conductive plastic surface. The surface of an article is pickled thereby. According to the invention, the article as a whole may be made of a plastic material. Also included according to the invention is an article having a surface of plastic. The plastic is, according to the present invention, free of particulate foreign matter, such as solid particles or crystallization particles. Preferably, the plastic surface to be pickled consists only of the non-conductive plastic.

Preferably according to the invention, but without limitation, the non-conductive plastic is selected from acrylonitrile-butadiene-styrene copolymer (ABS copolymer), polyamide (PA), polycarbonate (PC), mixtures of an ABS copolymer with at least one further polymer, and multicomponent plastics, such as glass-fiber reinforced plastics, such as PEEK (polyether ether ketone), ABS/PC, i.e., a component made of acrylonitrile-butadiene-styrene copolymer and polycarbonate (PC), especially selected from acrylonitrile-butadiene-styrene copolymer (ABS copolymer), polyamide (PA), polycarbonate (PC), and mixtures of an ABS copolymer with at least one further polymer.

ABS copolymers have polymer chains made from the monomers acrylonitrile, butadiene and styrene:



Previous methods are based on the principle that polybutadiene, in particular, is oxidatively attacked and removed. This is enabled, for example, by

chromosulfuric acid. However, it has been surprisingly found that it is possible to detach polystyrene moieties selectively from the surface of a plastic material to form cavities, which allow for subsequent plating. The solvents are also capable of dissolving polystyrene-like compounds, so that polyether ketones, such as PEEK, can also be treated with the process according to the invention, with an adapted aftertreatment.

If the non-conductive plastic includes ABS, the content of ABS should not be less than 20% by weight (100% by weight being the whole weight of the plastic). When the amounts are lower, sufficient cavities cannot be obtained on the surface, so that the plating may not be uniform on the surface. Depending on the desired result, this may be relevant.

Acetone and its derivative have proven to be particularly suitable pickling agents. Acetone is suitable because it dissolves polystyrene moieties effectively and selectively. Preferably, however, a derivative of acetone is used as a pickling agent, wherein said pickling agent has a higher flash point than that of acetone itself.

The flash point is the lowest temperature at which a vapor-air mixture above a substance can ignite.

The pickling process according to the invention is effected, in particular, at temperatures from room temperature (i.e., 20 °C) to 80 °C, preferably from 30 °C to 65 °C, especially from 40 °C to 60 °C. In this temperature range, the pickling is effective. The energy consumed for heating the pickling solution is acceptable from an economic point of view. At lower temperatures, the step of pickling also occurs, but the duration is so long then, that the process can no longer be integrated effectively into existing plating processes. At temperatures of above 70 °C, especially above 65 °C, or above 60 °C, the energy consumption is high, and the pickling is not more effective, so that the process is preferably performed in the mentioned temperature range.

In order to ensure safety during the process, the pickling agent has a flash point that is above the process temperature. Since the flash point of acetone is around -20 °C, specific safety precautions are necessary when acetone is used as

pickling agent. In order to avoid such additional cost and ensure the safety of the process, according to the invention, the pickling agent is preferably a derivative of acetone whose flash point is higher than that of acetone, preferably higher than 60 °C, especially higher than 65 °C, more preferably higher than 70 °C.

Suitable derivatives include, for example, acetophenone, benzalacetone, or 4-hydroxy-4-methyl-2-pentanone.

Mixtures of acetone with one or more of the mentioned derivatives may also be employed. Also, the process according to the invention includes that 2, 3 or more derivatives are employed in one mixture as a pickling agent. More preferably, only one acetone derivative is employed as the pickling agent. More preferably, the pickling agent is selected from acetone, acetophenone, benzalacetone, and/or 4-hydroxy-4-methyl-2-pentanone. These have a sufficiently high flash point and can also otherwise be integrated into existing plating methods under usual working safety conditions.

The concentration of the pickling agent in the pickling solution is preferably at least 0.01% by weight, based on the total weight of the pickling solution. It can be employed up to the solubility limit. Preferably, the concentration is from 1% by weight to 10% by weight, especially from 3% by weight to 5% by weight, respectively based on the total weight of the pickling solution.

According to the invention, the pickling solution is a solution in which the pickling agent according to the invention is dissolved in a solvent. The solvent may be any solvents in which the pickling agent is highly soluble. In addition, when selecting the solvent, it is to be taken care that the plastic surface should be well wetted, and that the pickling process can be integrated well into existing processes. Especially for the latter reason, the solvent of the pickling solution is selected from water and/or glycol and/or glycol compounds.

According to the invention, a glycol compound is selected from the group consisting of ethylene glycol, diethylene glycol, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monomethyl ether acetate, diethylene glycol

monopropyl ether acetate, butylglycol, ethylene glycol monobutyl ether, ethylene glycol diacetate, and mixtures thereof. Particularly preferred are diethylene glycol monoethyl ether acetate, ethylene glycol acetate, ethylene glycol diacetate, butylglycol, and mixtures thereof.

Thus, according to the invention, water alone, glycol alone, or a glycol compound alone can be employed as solvent. However, it is also possible to employ a mixture of water and glycol, a mixture of water and a glycol compound, or a mixture of glycol and a glycol compound. Mixtures of water, glycol and a glycol compound are also included according to the invention. More preferably, the solvent is water and/or glycol. Water is particularly preferred.

The pickling process according to the invention serves, in particular, for preparing surfaces for subsequent plating/metallization. Plating (or metallization – both terms have the same meaning in this invention) is usually carried out in an aqueous solution. If the solvent in the pickling process according to the invention is water, there is as little as possible contamination from foreign substances in the subsequent steps.

According to the invention, the pickling solution may also contain wetting agents in addition to the pickling agent and the solvent; wetting agents enable a particularly effective action of the pickling agent on the surface. Suitable wetting agents include, for example, surfactants, such as sodium olefinesulfonate, alkylbenzenesulfonates, or alcoholic compounds or glycol compounds as defined above.

In another embodiment, the pickling solution further includes precious metal compounds in a concentration of from 0.01 mg/l to 80 mg/l, preferably from 0.05 mg/l to 70 mg/l. Said precious metal is, in particular, a metal that is employed as an activator in the metallization. In particular, it is palladium. Suitable compounds for preparing activators, or activators themselves, are well known to those skilled in the art. A suitable compound for preparing activators is, for example, palladium chloride. Surprisingly, it has been found that this causes the later metallization to proceed particularly effectively. The pickling according to the invention changes the plastic surface in such a way that precious metals

and, in particular, palladium will adhere to the surface. This enables the subsequent metallization.

The plastic surface to be metallized or to be pickled is contacted with the process for pickling according to the invention for a period of from 0.1 to 60 minutes, preferably from 1 to 20 minutes, and more preferably from 6 to 12 minutes.

The process according to the invention enables polymer moieties to be detached from the surface of an article, which includes, in particular consists of, a non-conductive plastic material. It is believed that the detached polymer moiety is still connected with the remaining polymer moieties, and yet a formation of cavities occurs. It is believed that the precious metal, especially palladium, adheres in these cavities. As compared to conventional etching methods, more cavities having a lower depth are formed per surface area. Surprisingly, it has been found that a particularly homogeneous metallization can be achieved thereby.

If the polymer moiety detached by the pickling solution is to be removed from the surface, this can be done by an oxidative process in a preferred embodiment.

In a preferred embodiment of the process according to the invention, therefore, step b) includes the following substeps:

b1) the surface is contacted with a pickling solution, wherein said pickling solution contains a solvent and a pickling agent, and subsequently

b2) the surface is contacted with a permanganate solution.

Thus, in this embodiment, the process all in all includes the steps:

a) providing an article having a surface made of a non-conductive plastic material,

b1) contacting the surface with a pickling solution, wherein said pickling solution contains a solvent and a pickling agent, and subsequently

b2) contacting the surface with a permanganate solution, followed by

c) rinsing the surface to remove the permanganate solution,

wherein said pickling agent is capable of detaching polystyrene moieties from a polymer.

The permanganate solution does not have the effect of a pickling solution. The treatment with permanganate is effected after the pickling and merely serves for the oxidative cleavage of the polymer components detached by the pickling. Therefore, the permanganate solution preferably has a concentration of from 5 g/l to 200 g/l, especially from 10 g/l to 150 g/l, more preferably from 15 g/l to 100 g/l. In particular, the permanganate solution is an aqueous or alcoholic (ethanolic) solution.

In principle, the oxidative purification of the surface with the permanganate-containing solution (step b2 of the process according to the invention) can be effected in accordance with the prior art. For example, this step can be performed as described in EP 1 001 052 B1. In contrast to the prior art, there is no pickling by the permanganate in the present process according to the invention.

Accordingly, said permanganate solution may be in the form of an acidic solution, or in the form of an alkaline solution. Thus, the permanganate solution may contain, for example, an acid, especially sulfuric acid or phosphoric acid, or an alkali (base), especially potassium hydroxide or sodium hydroxide.

According to the invention, the surface may also be rinsed between steps b1) and b2) of the process preferred according to the invention. In particular, water is used as a rinsing means for rinsing the surface.

The rinsing in step c) is also performed with water, in particular.

If the process includes the oxidative treatment with a permanganate solution, this step is effected, in particular, at temperatures from room temperature (i.e., 20 °C) to 70 °C, preferably from 30 °C to 65 °C, especially from 40 °C to 60 °C.

In this temperature range, the pickling is effective. The energy consumed for heating the permanganate solution is acceptable from an economic point of view. The step of oxidative cleavage also takes place at lower temperatures, but the duration is so long then, that the process can no longer be integrated effectively into existing plating processes. At temperatures of above 70 °C, especially above 65 °C, or above 60 °C, the energy consumption is high, and the pickling is thus less cost-efficient, so that the process is preferably performed in the mentioned temperature range.

If the pickling process according to the invention includes the step of treating with an oxidative solution, especially with a permanganate solution, the concentration of the pickling agent can be decreased. In such cases, the concentration of the pickling agent in the pickling solution is, in particular, from 0.5% by weight to 5% by weight, preferably from 1% by weight to 4% by weight, more preferably from 1.5% by weight to 3% by weight, respectively based on the total weight of the pickling solution.

This offers advantages from an economic and ecological point of view, since the concentration of the individual ingredients can be reduced to the point where the process can be operated even less expensively as compared to the previously used chromosulfuric acid pickles. It is believed that, if the concentration in the pickling step containing acetone and/or an acetone derivative is lower than a certain threshold value, although uniform pickling (forming of microcavities) is achieved, loosely bonded residues remain therein, which are then removed in a subsequent, optionally oxidative, process, such as a weak permanganate solution.

Therefore, in a further embodiment, the present invention relates to an article having a surface of non-conductive plastic that contains polystyrene moieties, characterized in that the concentration of polystyrene at the surface is reduced. In a preferred embodiment, the surface is obtained by the process described above. As for the plastic, reference is made to the discussions relating to the process.

The pickling process according to the invention serves, in particular, for preparing surfaces for subsequent plating. In another embodiment, therefore,

the object of the present invention is achieved by a process for metallizing non-conductive plastic surfaces, characterized in that

in a first step, the surface is pickled by a process as disclosed above,

followed by plating the surface.

The metallization (plating) includes, in particular:

i) activation of the surface with an activator solution,

ii) especially electroless plating.

The process of plating as such can be effected by known methods. With the metallization process according to the invention, a process for metallizing non-conductive plastic surfaces is provided that is characterized by the pickling process according to the invention. All the following steps, such as activation, accelerating or also, optionally, direct metallizing, can be used or applied in the same form as with the previously used chromosulfuric acid pickles. In the metallizing step, nickel or copper layers, in particular, are applied to the layer of nuclei on the plastic surface.

The process steps of the present invention are performed in the stated order, but not necessarily in preferably direct succession.

Other process steps and additionally respective rinsing steps, preferably with water, but also with components, especially the solvents of the individual previous steps, can be performed between the respective steps.

The pickling of the plastic surface with pickling solutions according to the invention pickles the plastics so strongly and uniformly, that pickling alone in this step leads to sufficient adhesion of the metal layer applied.

The pickling of the plastics according to the invention with the pickling solutions according to the invention surprisingly leads to a significantly higher amount of coating on the surface with a metal during the activation of the surface. This

enables a reduction of the precious metal concentration employed during the activation, and thus enables a lower energy consumption.

Furthermore, the pickling process according to the invention can be used to coat far more plastics than was previously possible using chromosulfuric acid pickling, such as highly glass fiber-reinforced plastics like PEEK (polyether ether ketone).

This aspect also enables the opening-up of new and forward-looking fields of application, because even plastics with a metal-like stability can now be coated in a decorative or also functional way. Further, with the process according to the invention, the coating of multicomponent plastics is also possible in an even simpler way than previously. While both a further activation step and a further accelerating step were required in the prior art, i.e., pickling with chromosulfuric acid, presently no further adapted process steps as compared to the conventional procedure for the coating of such components are necessary.

Thus, the process according to the invention enables a simple and flawless coating independently of the type and concentration in the accelerator, and in the activator, whereby these are avoided as sources of error, and a significantly higher process safety is created. Therefore, in a further embodiment, the present invention relates to an article having a surface of non-conductive plastic, wherein said plastic contains polystyrene moieties, characterized in that the surface was metallized by a process as described above.

The following Examples show, in an exemplary and non-limiting way, a pickling process according to the invention, and a pickling solution, without, however, limiting the invention to the Examples. Features explained with respect to one embodiment also apply, *mutatis mutandis*, to all other embodiments, unless this is explicitly excluded.

Examples:

In all Examples, rinsing in water and optionally a wetting agent for better wetting was performed between the individual process steps, unless stated otherwise.

Example 1:

Pickling solution 1: 100 g/l benzalacetone, 300 ml/l butylglycol, 30 ml/l sodium olefinesulfonate (wetting agent)

Metallization

A plastic component made of ABC PC with a PC content of about 45%, also referred to as T45, was treated in the pickling solution from Example 1 at 50 °C for 5 minutes.

After the pickling, the plastic component had a uniformly roughened and easily wettable structure.

Example 2:

A plastic component made of ABC PC as used in Example 1 was treated as follows:

1. treat in pickling solution 1 at 50 °C for 5 minutes
2. treat in activator solution HESSOPLAST AKA from the company Dr. Hesse at 36 °C for 3 minutes
3. treat in accelerator solution HESSOPLAST BS-200 from the company Dr. Hesse at 35 °C and pH = 3.0 for 3 minutes
4. treat in chemical nickel solution HESSONIC PL-H from the company Dr. Hesse at 32 °C and pH = 8.5 for 9 minutes

HESSOPLAST AKA is a palladium activator with an exemplary composition in the activator solution of 25 mg/l Pd, 3 g/l Sn²⁺, and 300 ml/l HCl 37%.

HESSOPLAST BS-200 is an accelerator with an exemplary composition in the accelerator solution of 50 g/l HESSOPLAST BS-200, part 1, and 20 g/l HESSOPLAST BS-200, part 2, and in addition, the pH was lowered with sulfuric acid to pH = 3.0.

HESSONIC PL-H is an electroless depositing nickel method with an exemplary composition of 2.6 g/l Ni, 20 g/l sodium hypophosphite, about 30 g/l orthophosphite, and a stabilizer concentration of 3 mg/l.

The plastic component could be subjected to chemical nickel plating in a flawless and adhesion-strong way, followed by metallization.

Example 3:

Pickling solution 2: 30 g/l benzalacetone, 100 ml/l butylglycol, 30 ml/l wetting agent

Pickling solution 3: 50 g/l potassium permanganate, 50 g/l sulfuric acid 96% technical grade concentrated

Cleansing solution 1 (removal of manganese dioxide after pickling in permanganate-containing solutions): 50 ml/l sulfuric acid 96% technical grade concentrated, 50 ml/l hydrogen peroxide technical grade 33%

A plastic component made of ABC PC as used in Example 1 was treated as follows:

1. treat in pickling solution 2 at 50 °C for 4 minutes
2. treat in pickling solution 3 at 50 °C for 10 minutes
3. treat in cleansing solution 1 at 40 °C for 1 minute
4. treat in activator solution HESSOPLAST AKA from the company Dr. Hesse at 36 °C for 3 minutes

5. treat in accelerator solution HESSOPLAST BS-200 from the company Dr. Hesse at 35 °C and pH = 3.0 for 5 minutes

6. treat in chemical nickel solution HESSONIC PL-H from the company Dr. Hesse at 32 °C and pH = 8.5 for 9 minutes

The plastic component could be subjected to chemical nickel plating in a flawless way, followed by metallization.

Example 4:

Pickling solution 2: 30 g/l benzalacetone, 100 ml/l butylglycol, 30 ml/l wetting agent

Pickling solution 3: 50 g/l potassium permanganate, 50 g/l sulfuric acid 96% technical grade concentrated

Cleansing solution 2 (removal of manganese dioxide after pickling in permanganate-containing solutions): 20 ml/l hydroxylammonium sulfate.

A plastic component made of ABC PC as used in Example 1 was treated as follows:

1. treat in pickling solution 2 at 55 °C for 2 minutes

2. treat in pickling solution 3 at 55 °C for 10 minutes

3. treat in cleansing solution 1 at 40 °C for 1 minute
(no rinsing between step 2 and step 3)

4. treat in activator solution HESSOPLAST AKA from the company Dr. Hesse at 36 °C for 3 minutes

5. treat in accelerator solution HESSOPLAST BS-200 from the company Dr. Hesse at 35 °C and pH = 3.0 for 5 minutes

6. treat in chemical nickel solution HESSONIC PL-H from the company Dr. Hesse at 32 °C and pH = 8.5 for 9 minutes

The plastic component could be subjected to chemical nickel plating in a flawless way, followed by metallization. This also enables another shortening of the procedure, since the rinsing steps between step 2 and step 3 are omitted.

The pickling process found is advantageously compatible with most of the existing lines for metallizing plastics. It results in a more uniform roughening and nucleation of the plastic surface and thus in a faster and more flawless metallization, for example, in autocatalytic nickel plating. The results obtained are very well reproducible, and up-scaling of the metallization process from laboratory scale can be dispensed with.

CLAIMS:

1. A process for pickling non-conductive plastic surfaces, characterized by the steps of
 - a) providing an article having a surface made of a non-conductive plastic material,
 - b) contacting said surface with a pickling solution, wherein said pickling solution contains a solvent and a pickling agent, and
 - c) rinsing the surface to remove the pickling agent,wherein said pickling agent is capable of detaching polystyrene moieties from a polymer.
2. The process according to claim 1, characterized in that said non-conductive plastic is selected from acrylonitrile-butadiene-styrene copolymer (ABS copolymer), polyamide (PA), polycarbonate (PC), mixtures of an ABS copolymer with at least one further polymer, and multicomponent plastics, especially selected from acrylonitrile-butadiene-styrene copolymer (ABS copolymer), polyamide (PA), polycarbonate (PC), and mixtures of an ABS copolymer with at least one further polymer.
3. The process according to claim 1 or 2, characterized in that the solvent of the pickling solution is selected from water and/or glycol and/or glycol compounds, and especially is water.
4. The process according to at least one of claims 1 to 3, characterized in that said pickling agent is a derivative of acetone that has a higher flash point than that of acetone itself.
5. The process according to at least one of claims 1 to 4, characterized in that the following operations are performed in step b):

b1) the surface is contacted with a pickling solution, wherein said pickling solution contains a solvent and a pickling agent, and subsequently,

b2) the surface is contacted with a permanganate solution.

6. The process according to claim 5, characterized in that said permanganate solution is an aqueous solution of a permanganate.
7. The process according to claim 5 or 6, characterized in that the concentration of the permanganate solution is from 10 to 200 g/l.
8. The process according to at least one of claims 5, 6 or 7, characterized in that said permanganate solution is in the form of an acidic solution, or in the form of an alkaline solution.
9. The process according to at least one of claims 5 to 8, characterized in that said permanganate solution contains either an acid, such as sulfuric acid or phosphorus acid, or an alkali, such as potassium hydroxide or sodium hydroxide.
10. The process according to at least one of claims 1 to 9, characterized in that said rinsing of the surface in step c) of the process is effected with water.
11. The process according to at least one of claims 1 to 10, characterized in that the plastic is free of foreign matter, especially free of solid particles or crystallization particles.
12. An article having a surface of non-conductive plastic, wherein said plastic contains polystyrene moieties, characterized in that the concentration of polystyrene at the surface is reduced.
13. The article according to claim 12, characterized in that it was obtained by a process according to at least one of claims 1 to 11.

14. A process for metallizing non-conductive plastic surfaces, characterized in that

in a first step, the surface is pickled by a process according to at least one of claims 1 to 11,

followed by plating the surface.
15. The process according to claim 14, characterized in that the metallization (plating) includes:

i) activation of the surface with an activator solution,

ii) especially electroless plating.
16. An article having a surface of non-conductive plastic, wherein said plastic contains polystyrene moieties, characterized in that the surface was metallized by a process according to claim 14 or 15.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/065401

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C18/26 C23C18/20 C23C18/24
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007 100174 A (OKUNO CHEM IND CO) 19 April 2007 (2007-04-19) example 2 table 1 claims 1-5 paragraphs [0046], [0066], [0080] -----	1 - 16
X	US 3 445 350 A (KLINGER KENNETH A ET AL) 20 May 1969 (1969-05-20) column 5, line 5 - column 6, line 2 example VII table III claims 1,2,4,7,9,10,12,15 -----	1 - 4, 10 - 16
X	US 3 671 289 A (MAGUIRE EILEEN ET AL) 20 June 1972 (1972-06-20) claims 1-4,21 column 2, line 31 - column 4, line 72 -----	1 - 4, 10 - 16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 September 2024

Date of mailing of the international search report

01/10/2024

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Le Hervet, Morgan

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/065401

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