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(54) PROCESS FOR CLEANING ARTICLES AFTER ELECTROLYTIC AND/OR CHEMICAL SURFACE TREATMENT

(71) We, SCHERING AKTIENGESELLSCHAFT, a Body Corporate organised according to the laws of the Federal Republic of Germany, of Berlin and Bergkamen, Federal Republic of Germany, do hereby 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:—

The invention relates to a process for cleaning adherent aqueous solution from articles or objects after electrolytic and/or chemical surface treatment, preferably in order to recover the valuable substances contained in these agents.

Processes for rinsing electrolytically or chemically treated articles in order to clean them for subsequent treatments are already known. The sole treatment agent used for this purpose was water.

However, these processes have the disadvantage that they involve relatively great losses of the valuable substances, especially the metal salts, contained in the surface treatment agents.

Great efforts were therefore made to prevent, as far as possible, these losses of valuable metals and other treatment substances for economic reasons and, more recently, to preserve the environment.

Thus, the amount of water used for rinsing can be minimised by the known process of so-called spray rinsing and the use of multiple cascades. In addition, evaporation and volatilisation processes have also been used.

A technique widely used in electrolysing stations and in anodising, phosphatising and pickling plants is the recovery of the rinsing water by ion exchange means which operate in the circuit.

However, none of these processes gives satisfactory results.

Thus, according to the process first mentioned, the valuable metallic substances can be recovered in a relatively pure state only by means of a separate and expensive waste water conveying arrangement and chemical precipitation of hydroxide sludges. The disadvantage of the volatilisation and evaporation processes is that they involve a particularly high degree of energy consumption; the ion exchange columns bring about the formation of neutral salts that render the waste water detrimental to the environment.

Generally, it can also be established that none of the known processes permits an even remotely quantitative recovery of the valuable substances.

An object of the present invention is therefore to provide a process which permits both the thorough cleansing of objects or articles after the completion of surface treatment of the type in question and also a quantitative and technically simple recovery of the valuable substances adhering to the objects as a result of such treatment.

The present invention provides a process for cleansing adherent aqueous solution from articles or parts thereof after electrolytic and/or chemical surface treatment, wherein the articles or parts are treated with a water-immiscible liquid solvent containing one or more solvents and having a higher or lower density than the adherent aqueous solution.

In the process of the invention there is advantageously used as the water-immiscible liquid solvent one having a density of greater than 1.25 or less than 0.75. Preferably the solvent is incombustible, inert to the surface treatment agents used, non-toxic, and has a boiling point above 35°C.

Advantageously the solvent is a halogenated hydrocarbon, preferably a chlorofluorohydrocarbon, especially trichlorotrifluoroethane.

Advantageously the articles are treated in a device suitable for the purpose of the invention, preferably a rinsing chamber, especially a rinsing chamber provided with a cooling device. The solvent collecting in the lower portion of the rinsing chamber below or above the aqueous phase of the surface treatment agent is preferably drawn off and used again for the treatment of objects, or the aqueous surface treatment agent collecting in the lower portion of the rinsing chamber below or above the solvent is drawn off and, optionally after purification, preferably by filtration by means of active carbon, is used for further surface treatment.

The process according to the invention may be applied in all electrolytic and/or chemical surface treatment processes where it is necessary to purify and/or recover the aqueous solution still adhering to the objects after treatment.

The process of the invention is therefore suitable, in particular, for cleaning articles or objects treated with chemical or electrolysing baths, for example based on chromium, nickel, cobalt, copper, cadmium zinc, tin, lead, silver, gold or their alloys, in the case of which articles economic application and environmental demands require a recovery of the valuable substances that is as quantitative as possible.

These aims, which have hitherto been impossible to fulfil by any of the known processes, are now surprisingly achieved in a remarkable manner by the process according to the invention, in that this process renders possible, with a technically elegant procedure, both the thorough cleansing of objects treated in the manner described and also the straightforward quantitative recovery of the treatment agents naturally adhering to the objects after treatment.

The solvent must fulfil the conditions on the one hand of being water-immiscible and, on the other, of having a density sufficiently different from the adherent aqueous solution, that relatively rapid separation into two phases can take place.

Solvents which can be used according to the invention and which have these properties are, for example, trichlorotrifluoroethane and trichloromonofluoromethane.

Each of these solvent may be used alone or, if desired, mixed with one another.

The solvents are, in particular for purposes of safe application, to be preferably incombustible and have low, or preferably no, toxicity and the most corrosive surface treatment agents must be incapable of destroying them or destroy them only with great difficulty.

Advantageously the solvent should not have too low a boiling point or, if it does, it should be used in conjunction with suitable cooling devices.

Therefore, suitable solvents are those having boiling points of as much as possible above 35°C.

A wetting agent or a mixture of wetting agents must be added to the solvent to be used according to the invention, to reduce, if necessary, the surface tension and thereby to promote the downward migration through the solvent of the film of water on the treated objects.

For this purpose, depending on the desired aim, amphoteric, non-ionic, anion-active and cation-active wetting agents or mixtures thereof may be used, wetting agents containing fluorine or chlorine being particularly suitable.

The following may be mentioned by way of example:

Amphoteric wetting agents
N-lauryl-β-imino-dipropionic acid (Na-salt),
2-caprylimidazolinium-1-carboxymethyl-1-sodium ethoxylate,
lauroylamidopropyl-N-dimethylamino-acetic acid,
lauroylamidopropyl-N-dimethylamine oxide, and
cetyl diethylamino tetraglycol ether sulphate.

Non-ionic wetting agents
Nonylphenol polyglycol ether,
glycol distearate,
ethoxylated polypropylene glycol,
perfluoroctylsulphonamido-polyglycol ether, and
oleic acid amido polyglycol ether.

Anion-active wetting agents
Sodium lauryl sulphate,
perfluoroctylsulphonic acid (potassium salt),
coconut oil acid sarcoside (sodium salt),
dibutylnaphthalenesulphonic acid (sodium salt), and
o-phosphoric acid ester of oleyl octaglycol ether (triethanol-ammonium salt).

Cation-active wetting agents
Pentoxyethylstearylammonium chloride,
perfluoroctylsulphonamidopropyl-trimethylammonium iodide, and cetyltrimethylammonium bromide.

When cleaning articles or parts thereof treated with agents or baths containing chromic acid, it is necessary to use wetting agents which are inert to such agents or baths, particularly fluorine-containing wetting agents.

The treatment of articles or parts according to the process of the invention can be effected in a conventional apparatus suitable for this purpose, for example in a rinsing chamber. When using solvents with low boiling points, this chamber, as mentioned above, is advantageously provided with a cooling device which is also appropriate in the case of surface treatments taking place at relatively high temperatures, for example, with hot nickel baths.

When carrying out the process of the invention, the aqueous solution adhering to the articles after appropriate treatment processes is removed quantitatively by treatment with the solvent, that is, by sprinkling, spraying or pouring continuously or discontinuously, and can be collected in a container, the rinsing chamber itself being the most suited to this purpose.

Phase separation then takes place in the lower portion of the container or rinsing chamber, the solvent separating either above or below the adherent aqueous solution, depending on the specific weight of the solvent used.

The process of the present invention also ibcludes, on the one hand, drawing off the solvent by means of suitable devices such, for example, as pumps and connecting systems, and using it again for cleaning and, on the other, using the separated adherent aqueous solution agent for further surface treatment, optionally after purifying, preferably by filtration.

These measures therefore permit both the thorough cleansing of objects after completed surface treatment and also a quantitative recovery by a technically simple procedure of the valuable substances used.

Further advantages result from this in individual cases, for example, the possibility of constructing smaller surface treatment plants, for example, electrolysing plants, and the almost complete avoidance of waste water and thus the achievement of ideal environmental protection.

The following Examples illustrate the invention:

Example 1

Articles made of steel or iron, for example screws, were treated electrolytically at 5°C in an aqueous nickel electrolyte of conventional composition in a tank, then removed from the bath and transferred to a rinsing chamber. The articles were then sprayed with a solution consisting of trichlorotrifluoroethane (b.p.: 47.6°C, density 1.582 and 5 parts by weight of a wetting agent based on perfluoroctylsulphonic acid.

The spraying was effected at intervals with a total duration of 2 to 5 minutes whereby the nickeled parts were thoroughly cleansed of adherent bath solution.

Further articles were then cleaned in processes lasting several hours with a similar effect and at the same time the mixture, being formed, of the aqueous nickel electrolyte rinsed off the articles and the solvent/wetting agent solution, was collected in the lower portion of the rinsing chamber where immediate separation into two layers took place in each case. The lower solvent/wetting agent phase was then used, by means of a pump connecting system and a pipe connecting system, to feed the spray nozzles, and the upper aqueous electrolyte solution was fed to the tank with the nickel electrolyte after undergoing active carbon filtration.

The process involved no waste water and there were no appreciable electrolyte losses.

The experiment was repeated with equal success using a wetting agent based on ethoxylated polypropylene glycol.

Example 2

The process described in Example 1 was carried out using trichlorotrifluoroethane as the solvent without the addition of wetting agents. Although no wetting agents were involved, this experiment, too, resulted in satisfactory cleansing of the electrolysed articles. The solvent and the entrained electrolyte liquor were recovered practically quantitatively.

Example 3

The process described in Example 1 was carried out using a conventional weakly acidic zinc electrolyte. Trichlorotrifluoroethane containing, as the wetting agent, 3% by weight of cetyldiethylamino polyglycol ether sulphate was used as the solvent.

There was an optimum cleansing effect. After several days' operation electrolyte losses as a result of entrainment were not detected.

Example 4

The process described in Example 1 was carried out using a conventional alkaline, cyanide-containing zinc electrolyte. Trichlorotrifluoroethane, containing, as the wetting agent, 2% by weight of coconut oil acid sarcoside, was used as the solvent. The articles were free of any residue. It was possible to recover the solvent practically quantitatively for re-use.

WHAT WE CLAIM IS:—

1. A process for cleaning adherent aqueous solution from articles or parts thereof after electrolytic and/or chemical surface treatment, wherein the articles or parts are treated with a liquid water-immiscible solvent having a higher or lower density than the adherent aqueous solution, the water-immiscible solvent containing one or more wetting agents.

2. A process as claimed in claim 1, wherein the water-immiscible solvent has a density of greater than 1.25 or less than 0.75.

3. A process as claimed in claim 1 or claim 2, wherein the solvent is incombustible.

4. A process as claimed in any one of claims 1 to 3, wherein the solvent is inert to the surface treatment agents used.

5. A process as claimed in any one of claims 1 to 4, wherein the solvent is non-toxic.

6. A process as claimed in any one of claims 1 to 5, wherein the solvent has a boiling point above 35°C.

7. A process as claimed in any one of claims 1 to 6, wherein the solvent is halogenated hydrocarbon.

8. A process as claimed in claim 7,

wherein the solvent is a chlorofluorohydrocarbon.

9. A process as claimed in claim 8, wherein the solvent is trichlorotrifluoroethane.

10. A process as claimed in any one of claims 1 to 9, wherein the wetting agent is an amphoteric, non-ionic, anion-active and/or cation active wetting agent.

11. A process as claimed in claim 10, wherein the wetting agent is:

N-lauryl-β-imino-dipropionic acid (Na-salt),
2-caprylimidazolinium-1-carboxymethyl-1-sodium ethoxylate,
lauroylamidopropyl-N-dimethylamino-acetic acid,
lauroylamidopropyl-N-dimethylamine oxide,
cetyl diethylamino tetraglycol ether sulphate,
nonylphenol polyglycol ether,
glycol distearate,
ethoxylated polypropylene glycol,
perfluoroctylsulphonamido-polyglycol ether,
oleic acid amido polyglycol ether,
sodium lauryl sulphate,
perfluoroctylsulphonic acid (potassium salt),
coconut oil acid sarcoside (sodium salt),
dibutylnaphthalenesulphonic acid (sodium salt),
o-phosphoric acid ester of oleyl octaglycol ether (triethanolammonium salt),
pentoxyethylstearylammonium chloride,
perfluoroctylsulphonamidopropyl-trimethyl-ammonium iodide, or
cetyltrimethylammonium bromide,

or a mixture of any two or more of such compounds.

12. A process as claimed in claim 11, wherein the device is a rinsing chamber.

13. A process as claimed in claim 12, wherein the rinsing chamber is provided with a cooling device.

14. A process as claimed in claim 12 or claim 13, wherein the solvent collecting in the lower portion of the rinsing chamber below or above the aqueous phase of the surface treatment agent is drawn off and used again for treating the objects.

15. A process as claimed in claim 12 or claim 13, wherein the aqueous surface treatment agent collecting in the lower portion of the rinsing chamber below or above the solvent is drawn off and, optionally after purification, is used again for surface treatment.

16. A process as claimed in claim 15, wherein the aqueous surface treatment agent which is drawn off is purified by filtration through active carbon.

17. A process as claimed in any one of claims 1 to 16, wherein the objects have undergone treatment with a chemical or galvanising bath based on chromium, nickel, cobalt, copper, cadmium, zinc, tin, lead, silver, gold or an alloy of such metals.

18. A process as claimed in claim 1, substantially as described in any one of the Examples herein.

19. A process as claimed in any one of claims 1 to 18, wherein the valuable substances contained on the surface treatment agents are recovered.

20. Articles or parts thereof which have been cleaned by the process as claimed in any one of claims 1 to 18.

21. Metals or alloys whenever recovered by the process of claim 19.

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