United States Patent Office

3,032,435

Patented May 1, 1962

3,032,435

PROCESS FOR IMPROVING THE CORROSION RESISTANCE OF PIECES OF LIGHT METALS AND LIGHT METAL ALLOYS

Josef Martin Michel, Frankfurt am Main, Germany, assignor to Knapsack-Greisheim Aktiengesellschaft, Knapsack, near Koln, Germany, a corporation of Germany

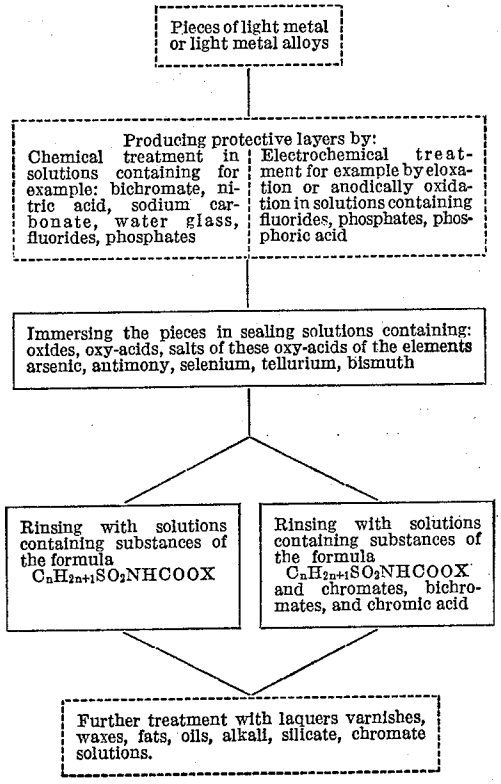
No Drawing. Filed July 13, 1959, Ser. No. 826,419
Claims priority, application Germany July 17, 1958
22 Claims. (Cl. 117—70)

The present invention provides a process for sealing and rinsing pieces of light metals and light metal alloys whose surfaces have been treated chemically or electrochemically and for simultaneously improving their resistance to wear and producing a protective effect which is "self-healing."

The protective layers that have been produced on pieces of light metals and light metal alloys by means of pickling solutions, by an electrolytic treatment or by the so-called contact process have in most cases to be subjected to an after-treatment directed to increase their resistance to corrosion.

The main purpose of such an after-treatment which may be carried out in various ways is to seal or close the pores still present in such a protective layer. The known methods of carrying out the after-treatment constitute exclusively physical processes consisting, for example, in greasing, waxing, oiling, lacquering, varnishing and the like, which may generally be applied, no matter what form the pieces have.

In contradistinction thereto, the present invention for the first time provides a process which is of purely chemical nature and which is suitable for the after-treatment of all sorts of protective layers applied to pieces of light metals and light metal alloys, no matter whether the protective layers have been produced by a chemical or an electrochemical process. Neither the structure nor the chemical composition of the primarily produced protective layer will exercise any influence on the invariably good effect of the after-treatment.



According to the process of the present invention for sealing pieces provided with the above-mentioned protective layers, the pieces are first dipped into strongly diluted solutions of oxides or oxide compounds of arsenic, antimony, selenium, tellurium and bismuth which are capable of being reduced to metals by light metals, the solutions being free from sulfur. At the places at which the protective layer is very thin or at which the metal is not at all covered with the protective layer the solution brings about a reaction in which the ion concerned is discharged and elementarily incorporated into the protective layer. As a consequence, the equivalent quantity of light metal dissolves according to the following equation which may be generally applied:

$$Me_I^{(2 \text{ to } 6)'} + Me_{II} \rightarrow Me_I + Me_{II}^{(2 \text{ to } 6)'}$$

A piece of a magnesium alloy provided in known manner with a layer of fluoride can, for example, be after-treated by the process of the invention in a solution of sodium selenite according to the following equation:

$$Se'''' + 2Mg \rightarrow Se + 2Mg''$$

Solutions of arsenic acid, antimonic acid, selenic acid, telluric acid, arsenious acid, antimonious acid, tellurous acid, in particular selenious acid and the salts thereof, have proved suitable. The after-treatment may, however, also be carried out successfully by means of mixtures of the aforesaid oxides or compounds thereof.

By this operation which in general takes but a few minutes the resistance to corrosion of the pieces and, in addition thereto, the resistance to wear of the protective layers are considerably improved.

The concentration of the solutions used for carrying out the after-treatment may vary within relatively wide limits, in general it should, however, not exceed 2% for otherwise there is a danger that the primarily produced protective layer will either partly dissolve or become spongy due to the absorption of too large quantities of metal.

In most cases the use of a solution of 0.5 to 1% strength of the above-mentioned oxides has proved particularly advantageous, the pH-value being suitably adjusted to about 5 to about 7, if desired by means of bases or compounds giving a basic reaction.

A passing over into the alkaline range should, if possible, be avoided and above all the pH-value should not be above 9.

The time of residence varies according to the concentration of the solution; the duration of the after-treatment can be decisively influenced by applying an appropriate temperature. In reactions taking place in two different phases, viz. a liquid and a solid phase, the structure of the primarily produced covering layer is also of importance because it is of decisive influence on the speed of diffusion of the solution in which the after-treatment is carried out.

Since the color of the protective layer changes in the course of the after-treatment the process can so to speak be traced colorimetrically. When, for example, a piece of magnesium alloys is treated in a selenium bath the coloration it acquires will vary, depending on the length of the period during which the piece is dipped into the solution between a light pink and a dark red. When pieces of eloxated aluminum are subjected to the same after-treatment light golden to coppery tints are obtained.

From what has been said follows that color effects of the aforesaid kind may, if desired, be made use of for purposes of decoration. For such a purpose not only the above-mentioned oxides and the salts thereof but also other agents having a similar effect are added to the solutions in which the after-treatment is brought about.

In order to accelerate the above-mentioned after-treatment the solutions used may, if desired, contain small quantities of alkali metal salts of strong or moderately strong acids, for example, sodium chloride, sodium phosphates, potassium fluoride and sodium sulfates, or mixtures of such compounds, these additives having the effect of regulating the acidity. In some cases, the addition of a minimum dose of the corresponding free acid proved to be advantageous.

In order to anchor the constituents incorporated in the protective layers by the process of the invention as firmly as possible, the portions of the bath still adhering to the layer should be washed out immediately after the after-treatment in order to be neutralized. This operation should above all be carried out in cases in which the oxide solution has been adjusted to a pH-value of 4.5 and less than 4.5. For the purpose of neutralizing the adhering portions of the bath the layer is first rinsed for a short time with tap water and finally treated in a solution having a pH-value of more than 7, preferably of between 7.5 and 8.5. It is advantageous to carry out the washing at an elevated temperature, preferably at a temperature within the range of 80° to 90° C. since the elevated temperature enables the pieces that have been treated to dry very quickly. As rinsing agents there may be used tap water having an alkaline effect and strongly diluted alkalies, for example, soda solutions (0.1% strength by weight and less), the addition of small quantities of hexavalent chromium ion in the form of chromic acid or chromates (1 gram per liter and less) being advantageous.

Further experiments have shown that the protective layers that have been after-treated as described above not only possess a high degree of resistance to corrosion and to wear, but in addition thereto the incorporated metal parts of arsenic, antimony, selenium, tellurium and bismuth have the effect of protecting the pieces at a distance, that is to say they have a "self-healing effect."

In cases in which for some reason or other, for example because of a subsequent treatment, parts of the base metal (magnesium or aluminum) are unprotected the aforesaid property still exercises a lasting, favorable effect, the property being especially important when water-bearing parts of heating and cooling systems are treated. The property is particularly favored by the metal parts which are distributed uniformly and, depending on the structure of the chemically or electrochemically produced protective layer, more or less densely in the form of a net all over the surface and which have a very small grain size amounting on an average to 2 microns.

It has also been found that the protective layers after-treated by the process of the invention are also accessible to a subsequent sealing which may be carried out in known manner by means of lacquers or varnishes, waxes, fats and the like. If it is desired to produce a purely inorganic protective layer it is advisable to carry out a final treatment by means of alkali silicate solutions which also results in a further improvement of the resistance to wear.

Experiments carried out in this connection have shown above all that the resistance to corrosion of the protective layers is further increased to a considerable extent, without any deterioration of the resistance to wear taking place, when the pieces are finally dipped into a thin aqueous or alcoholic solution of a metal-active organic compound of the general formula

$$C_nH_{2n+1}SO_2NHRCOOX$$

in which the number (n) of carbon atoms is preferably within the range of 12 to 18. As carboxylic acid containing an alkyl radical (R) there are preferably used acetic acid, propionic acid or butyric acid or mixtures of said acids. As salt-forming cation X there may, for example, be used sodium or the ammonium radical. In special cases it is, however, also possible to apply exclusively organic substances and to use, for example, the cyclohexyl amine salt of the aforesaid acids.

The following additional remarks remain to be made:

It is known to produce protective layers on light metals. The present invention does not relate to a process for producing protective layers but it is concerned with the after-treatment of protective layers, the preparation of the latter being taken for granted.

The inclusion of the after-treatment in the process of the pre-treatment, too, is a process which is different from the after-treatment according to the process of the invention which is carried out in a special stage after a known pre-treatment.

There are also known processes which are not directed to a pre-treatment resulting in the formation of a protective layer but to pickling operations in which the surface is only purified but in which no protective layer is produced. Processes of this kind are not relative, either, to the process of the invention.

According to the present invention, the process for sealing and rinsing pieces of light metals and light metal alloys whose surfaces have in a first stage been subjected to a known chemical or electrochemical treatment and for simultaneously improving their resistance to wear and producing a protective effect which acts at a distance consists in subjecting the pieces which have thus been pre-treated to an after-treatment for which purpose the pieces are first dipped in a second stage into a strongly diluted sealing solution of oxides or oxide compounds of arsenic, antimony, selenium, tellurium or bismuth which are capable of being reduced to metals by the action of light metals, said solution being free from sulfur, and after a washing with water the pieces are washed in a third stage at an elevated temperature in an alkaline liquid.

The aforesaid elements are present in the solution in quantities of at most about 2% weight, preferably in quantities within the range of about 0.5 to 1% by weight, in the form of the corresponding oxides or compounds thereof, the percentages being calculated on the total solution.

According to another feature of the invention the pH-value of the sealing solution is adjusted to at most about 9, preferbaly to about 5 to about 7, if desired by means of bases or compounds giving an alkaline reaction.

The rinsing solution may contain small quantities of preferably hexavalent chromium in the form of alkali chromates, alkali bichromates or chromic acid. Besides, aqueous or alcoholic solutions of substances of the general formula $C_nH_{2n+1}SO_2NHRCOOX$ may be added to the rinsing solution. In the aforesaid formula the number (n) of the carbon atoms contained in the alkyl radical is within the range of 12 to 18, R represents an alkyl radical of the first five members of the paraffin series and X represents an inorganic or organic cation bringing about the formation of a salt of the aforesaid sulfamide carboxylic acid. X may be a cation consisting of sodium, potassium, ammonium, an organic ammonium radical, for example, a radical of cyclohexyl amine, or the like.

The pH-value of the rinsing solution is kept above 7, preferably within the range of about 7.5 to 8.5. For this purpose there are, if necessary, used strongly diluted alkalies, for example, diluted soda solutions.

By adjusting the length of the period during which the pieces to be treated are dipped into the sealing solution which may, if desired, contain further additives colorations suitable for colorimetric or decorative purposes can be obtained. The sealing solutions may also contain small quantities of alkali metal salts of strong or moderately strong acids, for example, sodium chloride, sodium phosphates, potassium fluoride or sodium sulfate, or mixtures of such compounds or small quantities of the corresponding free acids, the additive being capable of regulating the acidity. It is also possible to add alkali chromates or bichromates or chromic acid to the sealing solution. In this case the rinsing solution can be dispensed with.

According to another idea of the invention an additional after-sealing can be carried out, for example in a fourth stage, by treating the pieces with lacquers, varnishes, waxes, fats, oils, alkali silicate solutions or other substances.

The temperature at which the pieces are treated in the sealing solution is preferably within the range of about +20° C. to about +70° C. and the temperature at which the pieces are treated in the rinsing solution is preferably within the range of about +70° C. to about +90° C. Depending on the temperatures applied, the duration of the treatment in the sealing solution is about 3 to about 10 minutes and that of the treatment in the rinsing solution about 5 to about 10 minutes.

As sealing solution there may, for example, be used solutions of arsenic acid, antimonic acid, selenic acid, telluric acid, arsenious acid, antimonius acid or tellurous acid, solutions of selenious acid being particularly suitable. As sealing solutions there may also be used solutions of the salts of the aforesaid acids or of bismuth or mixtures of the compounds that have been mentioned.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

Example 1

A sheet of a magnesium alloy containing 2% by weight of manganese was anodically treated in known manner in an alkaline solution. In order to bring about a subsequent sealing of the yellow-grey oxide layer that had formed the sheet was dipped for 10 minutes at room temperature into a solution containing 5 grams of selenious acid per one liter of distilled water. Subsequently, the sheet was rinsed with a hot solution (+80° to +90° C.) containing per liter 5 grams of the sodium salt of alkyl-sufamido acetic acid, the alkyl radical having a chain length of 12 to 16 carbon atoms.

When the resistance to corrosion was tested in a common salt solution of 3% strength by weight the sheet that had only been treated electrolytically exhibited spots of notable corrosion after 5 days already whereas the sheet that had been after-treated was altogether unchanged after the same time. The resistance to wear had been increased by the after-treatment from 9,000 to 18,000 units.

Example 2

A cast piece of an aluminum alloy containing 94% by weight of aluminum, 5% by weight of magnesium and 1% by weight of tin were treated in sulfuric acid of 10% strength by weight by the known process of eloxation with an alternating current. After having been rinsed with water the piece was dipped for about 5 minutes at +40° C. into a solution which per liter contained 2 grams of tellurous acid, 2 grams of sodium selenite and 1 gram of dipotassium phosphate. After this treatment the cast piece was dipped for about 10 minutes into a hot aqueous solution containing 7.0 grams of the cyclohexyl-amino salt of an alkyl sulfamide propionic acid, the carbon chain of the alkyl radical having a length within the range of 8 to 12. Contrary to other pieces that had not been after-treated the cast piece did not exhibit any phenomena of corrosion after having been sprayed for 3 weeks with sea-water.

Example 3

A cast piece of a magnesium alloy containing 6% by weight of aluminum and 3% weight of zinc was anodically treated in a saturated ammonium-fluoride solution. The piece that was provided with a white enamel-like protective layer was then dipped for 3 minutes into a solution heated to about +70° C., which contained 2 gram of arsenious acid and 2 grams of antimonious acid per liter of water and which had been adjusted to a pH-value of 6.5 by means of tertiary potassium phosphate.

The experiment was continued as described in Example 2. When the resistance to corrosion was tested in a common salt solution of 0.5% strength by weight it was found

that the piece that had not been after-treated was strongly corroded after one week already whereas after the same period the piece that had been subjected to an after-treatment did not exhibit any phenomena of corrosion after the same time.

Example 4

A sheet of a magnesium alloy containing 6% by weight of aluminum, 1% by weight of zinc and 0.5% by weight of manganese was anodically treated in an electrolyte containing 250 grams of ammonium fluoride and 150 grams of dipotassium phosphate per liter of water. The sheet was then treated for 3 minutes in a solution heated to +50° C. and containing 4 grams of sodium selenite and 1 gram of chromic acid per liter of tap water. Subsequently the piece was rinsed in the usual way.

By the after-treatment the resistance to wear of the layer had been increased from 2,300 to 17,000 units. Even after it had been subjected for several days to an alternate-immersion test in sea water no phenomena of corrosion could be observed.

Example 5

A piece of a magnesium alloy containing 6% by weight of aluminum and 1% by weight of zinc was pickled in known manner in a bath of bichromate and nitric acid containing 160 grams of potassium bichromate per liter of nitric acid of 20% strength by weight. The piece was then after-treated for 8 minutes in a solution which per liter of water contained 1 gram of sodium chloride in addition to 4 grams of selenious acid and which had been heated to about +35° C.

Whereas the layer of pure chromate was notably corroded after having been for 3 days in contact with common salt solution of 1% strength by weight the specimens which had been after-treated in the above-mentioned manner were completely unchanged. After another week a few places of the layer were corroded. However, when after having been subjected to the above-mentioned treatment and rinsed with cold tap water the cast piece was dipped for 5 to 10 minutes into a solution of about +70° C. containing per liter 10 grams of the ammonium salt of an alkyl sulfamide acetic acid having an alkyl radical of 12 to 18 carbon atoms and 10% by weight of glycol, the rest being tap water, no corrosion could be observed after a test period of three weeks.

Example 6

An injection-molded piece of a magnesium alloy containing 8.5% by weight of aluminum and 0.5% by weight of zinc was provided in a first stage by an anodical treatment in an electrolyte containing about 35 grams of phosphoric acid in addition to 350 grams of ammonium fluoride per liter of water with a white-grey enamel-like protective layer. After a short treatment with water the cast piece was dipped in a second stage for 2 minutes at room temperature into a solution containing 0.2% by weight of bismuth in the form of the complex ammonium citrate compound. During this treatment the protective layer turned a light grey.

After another rinsing with water the piece was dipped in a third stage for 5 minutes into a solution of 5% strength by weight of the ammonium salt of an alkyl sulfamido-acetic acid containing an alkyl radical of 12 to 18 carbon atoms. The solution had been heated to a temperature within the range of +60° C. to +80° C.

When the resistance to corrosion was tested by spraying with sea water the fluoride layer that had not been subjected to the after-treatment was notably corroded at several places after 3 days. At the end of the same test the cast piece of grey appearance which had been after-treated in a third stage in the above-mentioned manner did not yet exhibit any phenomena of corrosion.

I claim:

1. A process for forming a self-healing surface and for improving the resistance to corrosion of articles made of

light metal and light metal alloys, the surfaces of which have been pretreated to substantially seal the same, which comprises immersing the articles thus treated in a highly diluted condensation solution containing oxides of at least one element selected from the group consisting of arsenic, antimony, selenium, tellurium, and bismuth in quantities of at least about 0.5 to about 2% by weight of the total solution, said oxides being reduced by the light metal articles to metals, the rinsing articles with water and subsequently rinsing said articles with an aqueous solution of substances of the formula $C_nH_{2n+1}SO_2$ NHRCOOX, where n in the alkyl radical is 8 to 18, R is an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

2. A process as claimed in claim 1 wherein the elements are contained in the solution in a quantity within the range of about 0.5 to about 1% by weight calculated on the total solution.

3. A process as claimed in claim 1 wherein the pH-value of the sealing solution is adjusted to at most about 9.

4. A process as claimed in claim 3 wherein the pH-value of the sealing solution is adjusted to at most about 9 by means of at least one substance selected from the group consisting of bases and compounds giving an alkaline reaction.

5. A process as claimed in claim 1 wherein small quantities of hexavalent chromium in the form of at least one substance selected from the group consisting of alkali chromates, alkali bichromates and chromic acid are used in the subsequently applied rinsing solution.

6. A process as claimed in claim 1 wherein in the subsequently applied rinsing solution n is within the range of 12 to 18.

7. A process as claimed in claim 6 wherein alcoholic solutions of the subsequently applied rinsing solutions are used.

8. A process as claimed in claim 6 wherein X stands for an inorganic cation.

9. A process as claimed in claim 6 wherein X stands for an organic cation.

10. A process as claimed in claim 6 wherein X is a cation of at least one substance selected from the group consisting of sodium, potassium, ammonium and an organic ammonium radical.

11. A process as claimed in claim 1 wherein the pH-value of the subsequently applied rinsing solution is maintained within the range of about 7.5 to about 8.5.

12. A process as claimed in claim 1 wherein the pH-value of the subsequently applied rinsing solution is adjusted by means of dilute soda solution.

13. A process as claimed in claim 1 wherein the articles are subjected to a further treatment with at least one substance selected from the group consisting of lacquers, varnishes, waxes, fats, oils and alkali silicate solutions.

14. A process as claimed in claim 1 wherein the temperature at which the articles are treated in the sealing solution is within the range of about +20° C. to about +70° C. and the temperature at which the piece is treated in the subsequently applied rinsing solution is within the range of about +70° C. to about +90° C.

15. A process as claimed in claim 1 wherein depending on the temperatures applied the articles are treated for about 3 to about 10 minutes in the sealing solution and for about 5 to about 10 minutes in the subsequently applied rinsing solution.

16. A process for forming a self-healing surface and for improving the resistance to corrosion of articles made of magnesium and magnesium alloys which have been electrochemically pretreated in an electrolyte containing fluorine and phosphate ions which comprises immersing the treated articles in highly diluted condensation solutions containing oxides of at least one element selected from the group consisting of arsenic, antimony, selenium, tellurium, and bismuth in quantities of at least about 0.5% to about 2% by weight of the total solutions, said oxides being reduced by the magnesium to metals rinsing the articles with water, and subsequently rinsing the articles with an aqueous solution of substances of the formula $C_nH_{2n+1}SO_2NHRCOOX$, where n in the alkyl radical is 8 to 18, R represents an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

17. A process for forming a self-healing surface and for improving the resistance to corrosion of articles of aluminum and aluminum alloys which have been treated according to the known eloxal process which comprises immersing the treated articles in highly diluted condensation solutions containing oxides of at least one element selected from the groups consisting of arsenic, antimony, selenium, tellurium, and bismuth in quantities of at least about 0.5% to about 2% by weight of the total solutions, said oxides being reduced to metals by the aluminum, rinsing the articles with water, and subsequently rinsing the articles with an aqueous solution of substances of the formula $C_nH_{2n+1}NHRCOOX$, where n in the alkyl radical is 8 to 18, R represents an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

18. A process for forming a self-healing surface and for improving the resistance to corrosion of articles made of light metal and light metal alloys, the surfaces of which have been treated in known matter with at least one compound selected from the group consisting of sulphuric, nitric, chromic, phosphoric and oxylic acid, alkalies, chromates, fluorides, phosphates, water glass and sodium carbonate, with or without utilization of electric current which comprises immersing the articles thus treated in a highly diluted condensation solution containing at least one compound selected from the group consisting of oxides, oxy-acids and salts of the oxy-acids, an element selected from the group consisting of arsenic, antimony, selenium tellurium, and bismuth in quantities of at least about 0.5 to about 2% by weight of the total solution, rinsing the articles with water, and subsequently rinsing said articles with an aqueous solution of substances of the formula $C_nH_{2n+1}SO_2NHRCOOX$, where n in the alkyl radical is 8 to 18, R is an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

19. A process as claimed in claim 18 wherein the duration of the period of about 3 to about 10 minutes during which the piece is dipped into the sealing solution is adjusted in such a manner that the coloration of the piece obtained is suitable for purposes of colorimetry and decoration.

20. A process as claimed in claim 18 wherein a small quantity of at least one substance regulating the acidity and selected from the group consisting of alkali metal salts of strong acids, alkali metal salts or moderately strong acids and the free acids corresponding to said salts is added to the sealing solution.

21. A process for forming a self-healing surface and for improving the resistance to corrosion of articles made of magnesium and magnesium alloys provided in a first stage by an anodical treatment in an electrolyte containing fluorine and phosphate ions which comprises immersing the pretreated articles in highly diluted condensation solutions containing a compound selected from the group consisting of oxide, oxy-acids and salts of the oxy-acids, an element selected from the group consisting of arsenic, antimony, selenium, tellurium, and bismuth in quantities of at least about 0.5% to about 2% by weight of the total solution, said oxides being reduced by the magnesium to metal, rinsing the articles with water, and subsequently rinsing the articles with an aqueous solution of substances of the formula $C_nH_{2n+1}SO_2NHRCOOX$, where n in the alkyl radical is 8 to 18, R represents an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

22. A process for forming a self-healing surface and for improving the resistance to corrosion of articles of aluminum and aluminum alloys which have been treated according to the known eloxal process which comprises immersing the treated articles in highly diluted condensation solutions containing a compound selected from the group consisting of oxides, oxy-acids and salts of the oxy-acids, an element selected from the group consisting of arsenic, antimony, selenium, tellurium, and bismuth in quantities of at least about 0.5% to about 2% by weight of the total solutions, said oxide being reduced to metal by the aluminum, rinsing the articles with water, and subsequently rinsing the articles with an aqueous solution of substances of the formula $C_nH_{2n+1}NHRCOOX$, where n in the alkyl radical is 8 to 18, R represents an alkyl radical of the first five members of the paraffin series, and X is a cation for forming a salt of a sulphamido carboxylic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,988,012	Mason	Jan. 15, 1935
2,018,388	Tosterud	Oct. 22, 1935
2,313,753	Loose	Mar. 16, 1943
2,313,755	Loose	Mar. 16, 1943
2,785,098	Cunningham	Mar. 12, 1957
2,798,830	Newhard	July 9, 1957
2,846,343	Mason	Aug. 5, 1958
2,861,019	De Long	Nov. 18, 1958
2,880,148	Evangelides	Mar. 31, 1959
2,898,490	Damon	Aug. 4, 1959
2,930,106	Wrotnowski	Mar. 28, 1960

OTHER REFERENCES

Wernick et al. Metal Finishing, August 1956, pages 53–58.