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ANODIC COATING OF ALUMINUM

Otto Schaaber, Schorndorf, Wurttemberg, Germany, assignor, by mesne assignments, to Siegfried Junghans, Schorndorf, Germany

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The present invention relates to a novel method of the production of protective coatings upon aluminum and aluminum alloys and more particularly, to the production of novel oxide coatings upon aluminum or aluminum alloys during an anodizing treatment.

In the past many processes have been developed for the production of corrosion resistant coatings upon aluminum and aluminum alloys which depend in most cases upon the production of an oxide coating which is thicker than that ordinarily obtained by the oxidation of aluminum or aluminum alloys in air. In the production of such oxide coatings, two different types of processes have previously been developed, namely, chemical processes in which the oxide coatings are produced by the treatment of aluminum or aluminum alloys with special chemicals such as, for example, the treatment of aluminum or aluminum alloys with a boiling solution of soda and silicates; and electrolytic processes in which the aluminum or aluminum alloys are subjected to an anodizing treatment in aqueous solutions of sulfuric, chromic or oxalic acid.

The exact constitution of the coatings produced by the previously known processes is not entirely clear. However, it is generally accepted that such processes depend upon the production of hydroxide coatings which are later transformed into oxides either by naturally or artificially induced ageing. The recent investigations of R. Fichter, *Helv. Phys. Acta* 19, 21 (1946) clearly indicates that such hydroxide formation takes place even in the previously employed electrolytic processes, while hydroxide formation in the chemical processes has previously been determined by chemical analysis.

During the heating of aluminum or aluminum alloys in air or in salt baths commonly used in the heat treatment of aluminum or aluminum alloys, a very thin oxide coating is obtained. The oxide coating produced in the salt baths is usually spoken of as a nitride coating and is thought to render it difficult subsequently to apply anodic coatings and is consequently normally removed before the aluminum is subjected to anodic treatment. These oxidic coatings do not contain hydroxide in view of the high temperatures at which they are formed, but they are not suitable for practical purposes as they are not thick enough.

It is an object of the present invention to provide a novel process for the production of oxide coatings upon aluminum or aluminum alloys which do not contain any hydroxides and which are substantially poreless, which oxide coatings

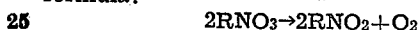
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are of the same thickness as the previously artificially obtained coatings.

It is a further object of the invention to provide a process for coating aluminum or aluminum alloys which may be carried out in conjunction with heat treatment of such aluminum or aluminum alloys in salt baths which normally contain alkali metal nitrates while avoiding disturbing surface alterations of such aluminum and aluminum alloys.

In accordance with the present invention, it has been discovered that corrosion resistant substantially poreless oxide coatings which are free of hydroxides may be obtained upon aluminum and its alloys if aluminum and its alloys are subjected to anodic oxidation, in substantially water-free fused salt baths of such composition that they liberate oxygen at the anode upon electrolysis. Salt baths primarily containing nitrate or nitrite salts or mixtures of both are preferably employed.

In the electrolysis of nitrate-containing baths, the reaction may follow the following general formula:



wherein R is a monovalent metal radical. The course of the reaction is probably more complicated than indicated above, and it must be assumed that the reaction proceeds further, for even in fused nitrite-containing salt baths coatings will be produced in accordance with the invention which, while they may not be as thick as those obtainable in nitrate-containing baths, are corrosion resistant. It is believed that the reaction in nitrite-containing baths may follow the following general equation:



In the electrolysis of nitrate-containing salt baths at very high current densities of, for example, 5 amp./dm.², the evolution of brown gases in addition to oxygen can be observed, and it may be assumed that in such case NO₂ is produced in accordance with the following equation:



The equations given above are obviously not complete, as they do not take the aluminum which enters the reaction into consideration.

The coatings which may be obtained in accordance with the invention possess many advantages over the coatings produced by the previously known processes in that substantially clear transparent coatings may be produced even with aluminum alloys containing less than 99.5% Al and

in that they are substantially pore-free. The process in accordance with the invention also has the advantage that it may be combined with a heat treatment of the aluminum to be coated and furthermore that such process prevents a deleterious attack of the aluminum surfaces during the heat treatment in fused salt baths.

The fused salt baths employed in accordance with the invention as the electrolytes for the anodic coating process are preferably essentially composed of alkali metal (including ammonium) nitrates or nitrites or mixtures of such nitrates and nitrites. Sodium and potassium nitrates and nitrites have been found especially well suited for the process. Ammonium nitrates and nitrites are also suited but are not as practical as they tend to vaporize. The relatively non-expensive sodium and potassium nitrates which respectively have melting points of 310° C. and 337° C. are well suited as electrolytes in accordance with the invention. Potassium dichromate has also been found suitable.

The special properties of the coatings produced in accordance with the invention are believed to a certain degree to be caused by the relatively high temperatures of the salt baths during the electrolysis.

Transparent glass-clear coatings may be obtained upon pure aluminum and when special precautions are observed, which will subsequently be described in detail, such transparent coatings may also be obtained upon aluminum alloys. No pores are visible in the coatings obtained in accordance with the invention, even upon inspection by high powered microscopes even up to the limits of resolution of light microscopes. The coatings may in some instances contain very fine cracks whose incidence depends upon the manner in which the coated articles are cooled when withdrawn from the fused electrolytes. These cracks are evidently caused by the difference in the coefficients of expansion of the base metal and the coating. These cracks only occur noticeably when the articles are quenched in cold water and may be substantially avoided when the articles are cooled slowly, such as, for example, in air.

A special characteristic of the process in accordance with the invention is that evidently during the electrolysis special layers occur in the bath at the cathode and anode, for the current flow decreases during the electrolysis and when a voltmeter is connected to the electrodes after the current is cut off, the anode, namely, the aluminum being treated, shows a local element potential of 2 to 2.5 volts again as the anode. This potential rapidly falls off and is reduced to under 0.5 volt in about a minute, and at the same time the gas bubbles which are still produced at the anode after the current is cut off decrease. If, for example, pure aluminum is electrolytically treated in accordance with the invention with a direct current initially having a current density between 5 to 10 amp./dm.² at ten volts, the current flow rapidly decreases and after one minute of electrolysis is only 0.8 amp./dm.². However, if the electrolyzing current is cut off for about a minute and is turned on again, the current flow is raised to between 3 and 6 amp./dm.², this current flow, however, again decreases rapidly but can be brought up again by interrupting the electrolyzing current flow.

It has been found advantageous to add catalytic materials to the nitrate-containing electrolytic baths employed in accordance with the

invention, which materials act to increase the rapidity of the oxidation of the aluminum. For example, it has been found advantageous to add small quantities of copper and iron compounds to the baths before they are used as electrolytes in accordance with the invention. These may be easily introduced by sending a direct or alternating current through the bath employing iron or copper electrodes whereby iron or copper compounds are introduced into the baths which, after a period of time, evidently are converted to their oxides. It is also known that the reduction of nitrates may be catalytically accelerated by the presence of copper or lead oxides. Also the introduction of a small quantity of copper nitrate into the electrolytic baths has been found to produce a similar effect. Furthermore, the presence of nitrites accelerated the reduction of nitrates in the bath. All these materials evidently have the effect that the local element potential at the anode degenerates more rapidly and that the current stays at higher values for longer periods of time. This is very important for the appearance of the coating produced upon all aluminum alloys. For example, if aluminum of 99% purity is anodized in accordance with the invention employing only 8 volts and an initial current density of 3 to 4 amp./dm.² in a sodium nitrate bath at 350° C. the coating obtained is dark colored. This coloration is caused, as may be seen from microscopic study, by the alloying elements which separate out at the edges of the grains and color under the influence of the electric current. If higher initial current densities are used the aluminum oxide coating is evidently produced so rapidly that the alloying elements present at the edges of the grains are covered and separated from the direct influence of the electrolyzing current. This aforementioned coloration does not substantially affect the corrosion resistant properties of the coating obtained, and consequently the following precautions need only be observed in carrying out the process in accordance with the invention upon aluminum alloys, if a light metal tone is desired upon the alloys treated.

One method of insuring the production of light transparent coatings upon aluminum alloys is to degenerate the local element effect by periodically cutting off the electrolyzing current so that a high average current density is obtained as indicated above. For example, a light colored coating is produced upon an aluminum alloy of the constitution 24S when treated as follows: a sheet of such alloy which has been pretreated by normal etching in caustic soda, followed by dipping in nitric acid and drying, is dipped into a fused salt bath composed of sodium nitrate and a small amount of sodium nitrite. If the sheet has been completely defatted the electric anodizing current flow can be instituted immediately, however, should bubbles occur on the sheet due to the presence of traces of fat thereon, it is advisable to destroy the bubbles by withdrawing the sheet from the bath and allowing the salt coating to solidify before instituting the anodizing treatment. An anodizing current of eleven volts is used and is preferably initially permitted to flow only for about one to ten seconds and is then interrupted until the voltage occurring at the aluminum, when measured by a voltmeter, has degenerated to one-half its original value when the anodizing current was cut off, or one can continue the interruption of the external anodizing current flow until no noteworthy bubble for-

mation takes place upon the aluminum. Preferably the period during which the external anodizing current is cut off is at least as long as the period during which such current is on. This sequence of switching on and off of the anodizing current is continued until 0.05 to 0.1 kwh./m.² have been consumed when direct current is used for the anodizing current.

This interrupted anodizing is expediently effected by anodizing a plurality of aluminum articles in one electrolyzing bath and sequentially supplying the anodizing current to each article, so that the load upon the source of current remains substantially constant. When the on period for the current is about five seconds, and the off period is about fifty-five seconds, twelve articles can be arranged to be anodized in the bath with one cathode and supplying the anodizing current to each article for five seconds every minute with a rotating distributor.

The interrupted anodizing current may also be produced by the discharge of suitable condensers. The desired interruption of the anodizing current may also be achieved by withdrawing the article treated from the bath.

It is also possible to employ a pulsating direct current, that is, a current that pulses between 0 and the desired voltage. The local element effect is constantly weakened by the constant pulsation between 0 volt and the desired voltage. If the local element voltage of 2 to 2.5 volts is to be completely degenerated, a current may be employed which fluctuates between -2 volts and the desired voltage. This type of current may be provided by superimposing a direct current of (N-2) volts upon an alternating current of N volts. For example, if a direct current of 8 volts is superimposed upon an alternating current of ten volts, the voltage at the anode side of the direct current will fluctuate between +18 and -2.

It is also possible to employ alternating current for the process in accordance with the invention. Protective coatings are obtained which are of the same thickness as the coatings obtained with direct current, but the current used in obtaining them is somewhat greater than when direct current is used because of slight disintegration of the coating being produced during the negative phase. In certain instances, the use of alternating current or alternating current followed by direct current has been found advantageous. For example, a bright rolled aluminum sheet having deep grooves which are very difficult to clean is advantageously first treated with an alternating current and then subjected to a normal direct current treatment. The corrosion resistance obtained is substantially better than when only direct current has been used. This is probably caused by the cleaning action upon the surface obtained with the alternating current for during the negative phase alkali is found at such surface.

The voltage employed for the process in accordance with the invention should preferably not be below ten volts for otherwise too little current will flow because of the resistance of the electrolytic bath. Preferably the voltage used should not exceed about fifty volts to avoid the production of rough and dull coatings which are obtained when the voltage is high enough to cause dielectric breakdown in the coating produced.

The consumption of current for the production of a corrosion resistant coating in accordance with the invention is about 0.1 kwh./m.² when direct current is used. This very low current consumption may be explained in that the

current flow decreases very rapidly from its high initial value of about 5 to 25 amp./dm.² (depending upon the voltage used and the distance between the electrodes). For example, with pure aluminum, using a sodium nitrate-potassium nitrate mixture as the electrolytic bath, it was found that after one minute the current flowing through the layer formed was only about 1 amp./dm.² and after five minutes, below 0.2 amp./dm.².

The temperature of the fused bath which is employed as electrolyte depends upon the use to which the aluminum or aluminum alloy is to be put. It can vary between about 140° C. and the temperature at which the aluminum or aluminum alloy melts. It has been found preferable for some purposes to maintain the temperatures of the salt baths between 300° C. and 550° C., as corrosion resistance is increased at these higher temperatures.

The process in accordance with the invention may, for example, be combined with a homogenizing heat treatment. An Al-Mg-Cu alloy corresponding to alloy 24St may be provided with a glossy corrosion resistant coating and simultaneously be subjected to a homogenizing heat treatment in the following manner. The alloy was immersed and anodized in a bath of fused sodium nitrate containing a small quantity of potassium nitrate and sodium nitrite (about 5%) which was maintained at a temperature of 500° C. to provide the homogenizing temperature. In order to avoid blackening of the coating, the anodizing current was supplied in surges of one to two seconds, with intermediate rest periods of about twenty seconds, and the anodizing treatment continued until the current consumption was about 0.2 kwh./m.². The current used was fifty cycle alternating current of about twenty volts. The current was switched on and off on the primary side of the transformer used in supplying the current.

The process in accordance with the invention may also be combined with an artificial ageing of aluminum alloys. For example, an Al-Mg-Si sheet may be aged at, for example, 175° C. in a bath composed of sixty parts potassium nitrate and forty parts sodium nitrate, and while in such bath anodized in accordance with the invention for six minutes without interruption with a direct current of eleven volts. Ammonium nitrate could also be used in the bath at these temperatures, but it evaporates rapidly.

The aluminum or aluminum alloys which are to be subjected to the anodizing treatment in accordance with the present invention may be subjected to the same pretreatments which are customary in the previously employed anodizing processes. It has, however, been found that in most instances a short etching in a caustic soda solution of about 5% to 15% concentration which is not too hot is sufficient. If the articles to be treated have a smooth polished surface, it is normally only necessary to defat such surfaces before treatment. Etching of the aluminum surface is not observed during the treatment in accordance with invention as customarily occurs during the previously employed anodizing processes employing aqueous electrolytes. To the contrary, it has been found that the present process results in the disappearance of etched surfaces under the clear coating which is obtained. On lightly etched pure aluminum, it may be readily seen that the coating produced

in accordance with the invention has a pronounced glossing effect.

As the coating obtained with the present process is free from pores, it is unnecessary to subject the treated articles to a sealing process such as is normally necessary after the previously employed anodizing processes. Even though the coatings contain no pores, they have been found to provide a good bond for lacquer coatings, if these are desired. It is also possible to boil the articles coated in accordance with the invention in a 2% to 5% waterglass solution to increase their corrosion resistance.

The corrosion resistance of the coatings obtained in accordance with the invention is excellent. A drop of concentrated HCl will dry upon a clean coating produced according to the invention upon pure aluminum or upon Al-Cu-Mg and Al-Mg-Si alloys without the formation of bubbles. The corrosion resistance of the coatings produced in accordance with the invention may also be seen from the following comparative tests:

Test samples were coated in accordance with the invention and compared with samples of the same alloy anodically coated in an aqueous 30% sulfuric acid solution and sealed with nickel acetate. The samples were immersed for one hour at 20° C. in an acid solution containing one part concentrated HCl, four parts concentrated HNO₃ and four parts distilled water. The following table shows the weight losses of the samples in grams per square meter. Column A gives the values for the samples treated in accordance with the invention and column B gives the values for the samples treated in aqueous sulfuric acid and sealed with acetate.

	A	B
(a) Alloy: Al-Cu-Mg.....	6.48 4.64 11.64	82.5
(b) Alloy Al-Mg-Si.....	0.1	61.5

¹ This sample had been subjected to treatment with a water glass solution after anodizing.

A further comparison of the corrosion resistance of the coatings produced in accordance with the invention and those produced in aqueous 30% sulfuric acid and sealed with acetate may be seen from the table given below which shows results from longer corrosion tests in which the samples were immersed for 113 hours at 20° C., in a solution composed of 3% NaCl, 0.5% HCl and the remainder distilled water. The values are given in table in weight loss in grams per square meter per hour, column A giving the values for the samples coated in accordance with the invention and column B giving the values for the samples treated in aqueous sulfuric acid and sealed with acetate:

	A	B
(a) Al-Cu-Mg alloy.....	0.118	0.914
(b) Al-Mg-Si alloy.....	0.064	1.06

Tests were also carried out to show the difference obtained, when different types of current were employed in producing a coating in accordance with the present invention. These test samples were all of pure aluminum which was bright rolled but still contained deep grooves caused by a defective hot roll. The solution used for the corrosion test was the normal ox-

dizing acid solution used for testing corrosion resistance to acid canned goods, namely, one composed of 2.5% NaCl, 1.5% concentrated acetic acid, 0.1% H₂O₂ and the remainder distilled water. The solution was renewed on the fourth, sixth, ninth and twelfth days, and the total duration of the test was sixteen days. The anodizing treatment employing a fused sodium nitrate bath for the various samples tested is as follows:

Sample No.	Anodizing treatment
122.....	6 minutes with 20 volt alternating current.
123.....	1 minute without current for 5 minutes with 20 volts' alternating current.
124.....	6 minutes 20 volt alternating current, 5 minutes 10 volt direct current.
125.....	10 minutes of interrupted 10 volt direct current in which current was supplied in 5 second surges with 50 second pauses between such surges.
126.....	6 minutes 10 volt direct current interrupted 4 times for about 5 seconds.

The values given in the table are the total losses in grams per square meter.

Sample No.	After 4 days	After 6 days	After 9 days	After 12 days	After 16 days
122.....	2.92	4.46	6.70	10.61	13.58
123.....	4.07	9.71	14.6	33.65	44.6
124.....	0.39	1.10	2.04	3.78	6.30
125.....	0.78	1.65	2.91	4.76	7.67
126.....	0.78	2.23	3.78	19.04	14.93

¹ Sample 126 was damaged with two scratches on the ninth day, and the excess attack occurred at these scratches.

The surfaces of samples 124, 125, and 126 were practically unchanged after sixteen days, but the samples showed corrosions at the cut edges which gradually became deeper and apparently the weight losses observed were caused by these.

The process in accordance with the invention has been found of special advantage in the treatment of copper-containing aluminum alloys. Such alloys upon such treatment with a caustic soda etch show a dark coating which may be wiped off, but which is preferably dissolved with dilute HNO₃, before anodizing with the previously employed anodizing processes employing aqueous solutions. It has been found unexpectedly that this dark colored coating need not be removed when the coating process in accordance with the invention is employed. When employing the present coating process, it is only necessary to dry the articles and then to anodize them in the water-free fused salt bath. The surfaces are still dark upon removal from the anodizing bath, but this darkness disappears when the anodized articles are rinsed with water.

It is also possible to produce colored oxide coatings with the process in accordance with the invention by the addition of special substances to the electrolytic bath. For example, the addition of 1% to 50% of sodium or potassium dichromate to the fused electrolytic bath will cause light yellow to deep brown coloration of the oxide coating. Deep black oxide coatings may be obtained by the addition of very small quantities of crystallized citric acid to the fused electrolytic bath. Additions of 0.1% to about 2.5% have been found suitable. The addition initially causes foaming of the bath. The coating obtained is uniformly black throughout its entire thickness even under a microscope. The corrosion resistance of the colored coatings obtained with dichromate and citric acid additions are substantially equal to those obtained without such additions.

While the invention has been described with particular reference to fused nitrate and nitrite baths, it is obvious that other fused salt baths may be employed as long as such baths have the proper melting point and boiling point, are substantially anhydrous and upon electrolysis will liberate oxygen at the anode. Fused salt baths which attack aluminum to a substantial degree should be avoided. Potassium dichromate has been found well suited for providing corrosion resistant coatings upon aluminum base metals in accordance with the invention. For example, an Al-Cu-Mg alloy was anodized in a fused bath of potassium dichromate at a temperature of 400° C., employing a voltage of eleven volts. The total time of treatment was a little less than one hour, but the current was interrupted several times for substantial periods so that the total electrolyzing time was less than thirty minutes. A sample of the coated alloy was submitted to a corrosion test in four parts distilled water, four parts concentrated nitric acid and one part concentrated hydrochloric acid. The weight loss of the sample amounted to 0.42 gram per hour per square meter. Also another sample of the same alloy was anodized for ten minutes at eleven volts in a fused dichromate bath at a temperature of 500° C. A sample of the coated alloy showed a loss of 1.35 grams per hour per square meter in the same mixture of acids.

I claim:

1. A process for the production of an oxidic coating upon an aluminum base metal which comprises anodizing such aluminum base metal with direct current in a substantially water-free fused salt bath essentially consisting of at least one alkali metal nitrate and at least one alkali metal nitrite as the electrolyte, the anodizing current being intermittently supplied and the anodizing voltage being up to 50 volts, the individual periods of supply being from 1 to 10 seconds duration and the periods during which current is not supplied being at least as long as the periods in which the current is supplied.

2. A process for the production of an oxidic coating upon an aluminum base metal which comprises anodizing such aluminum base metal in an electrolytic cell with direct current in a substantially water-free fused salt bath essentially consisting of at least one alkali metal nitrate and at least one alkali metal nitrite as the electrolyte, the anodizing current being periodically interrupted and the anodizing voltage being up to 50 volts, the periods during which the anodizing current is not supplied being sufficiently long that the cell voltage continuing after the anodizing current is interrupted falls to at least one half the value of such voltage when the anodizing current is first interrupted.

3. A process for the production of an oxidic coating upon an aluminum base metal which comprises immersing said aluminum base metal in a substantially water-free fused salt bath es-

entially consisting of at least one alkali metal nitrate and at least one alkali metal nitrite and supplying an anodizing current to said immersed aluminum base metal which anodizing current periodically varies from a voltage between -2.0 volts and 0 volt to a positive anodizing voltage up to 50 volts, the fused salt bath being maintained at a temperature between 140° C. and the melting point of the aluminum base metal during the treatment with the anodizing current.

4. A process in accordance with claim 3, wherein the temperature of the fused salt bath is maintained between 350° C. and 550° C. during the treatment with the anodizing current.

5. A process in accordance with claim 3, wherein said fused salt bath also contains a catalyst which accelerates decomposition of nitrates.

6. A process in accordance with claim 3, wherein said fused salt bath also contains a relatively small quantity of an iron compound.

7. A process in accordance with claim 3, wherein said fused salt bath also contains a relatively small quantity of a copper compound.

8. A process for the production of oxidic coatings upon an aluminum alloy containing copper which comprises etching such alloy in an alkali metal hydroxide solution whereby a dark colored coating is formed on such alloy, immersing said aluminum base metal in a substantially water-free fused salt bath essentially consisting of at least one alkali metal nitrate and at least one alkali metal nitrite without first removing such dark colored coating and supplying an anodizing current to said aluminum base metal carrying said dark colored coating which anodizing current periodically varies from a voltage between -2.0 volts and 0 volt to a positive anodizing voltage up to 50 volts.

9. A process in accordance with claim 3 wherein the fused salt bath also contains 1% to 50% of an alkali metal chromate.

10. A process in accordance with claim 3 wherein the fused salt bath has 0.1% to 2.5% of citric acid added thereto.

OTTO SCHAABER.

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