

[54] **PROCESS FOR THE PRODUCTION OF ALUMINUM BASE OFFSET PRINTING PLATES**[75] Inventors: **Shiro Terai**, Nagoya; **Toshio Suzuki**, Kasugai; **Yoshikatsu Hayashi**, Nagoya, all of Japan[73] Assignee: **Sumitomo Light Metal Industries Limited**, Tokyo, Japan[22] Filed: **Apr. 5, 1972**[21] Appl. No.: **241,202**[30] **Foreign Application Priority Data**

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Primary Examiner—Thomas Tufariello
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[57] **ABSTRACT**

This invention relates to a process of producing an aluminum base offset printing plate including a step wherein the surface of an aluminum base sheet is roughened or grained electrolytically by treating with alternating electric current at a current density of a selected range in an aqueous electrolyte containing hydrogen chloride as the primary etching agent and in the presence of one or more anti-corrosive agents chosen from some selected primary alkyl amine, secondary alkyl amines and tertiary alkyl amines, either unsubstituted or substituted by carboxyl or hydroxyl on the alkyl group(s), alkylene diamines, alkyl aldehydes, alkanolic acid amides, urea, chromic acid and known ionic surface-active agents. The presence of the anti-corrosive agent results in an improved uniformity of the grain particle size and prevents the dark colored aluminum smutt from depositing on the grained surface. The electrolytically graining treatment may continuously be performed with a continuous aluminum strip when an electrolytic cell of a particular arrangement as shown in the accompanying drawings is employed and when the treatment is effected in the presence of a mono-alkanol amine, di-alkanol amine, tri-alkanol amine or non-ionic surface active agent derived from polyethylene-glycol as the anti-corrosive agent under particularly more favorable etching conditions.

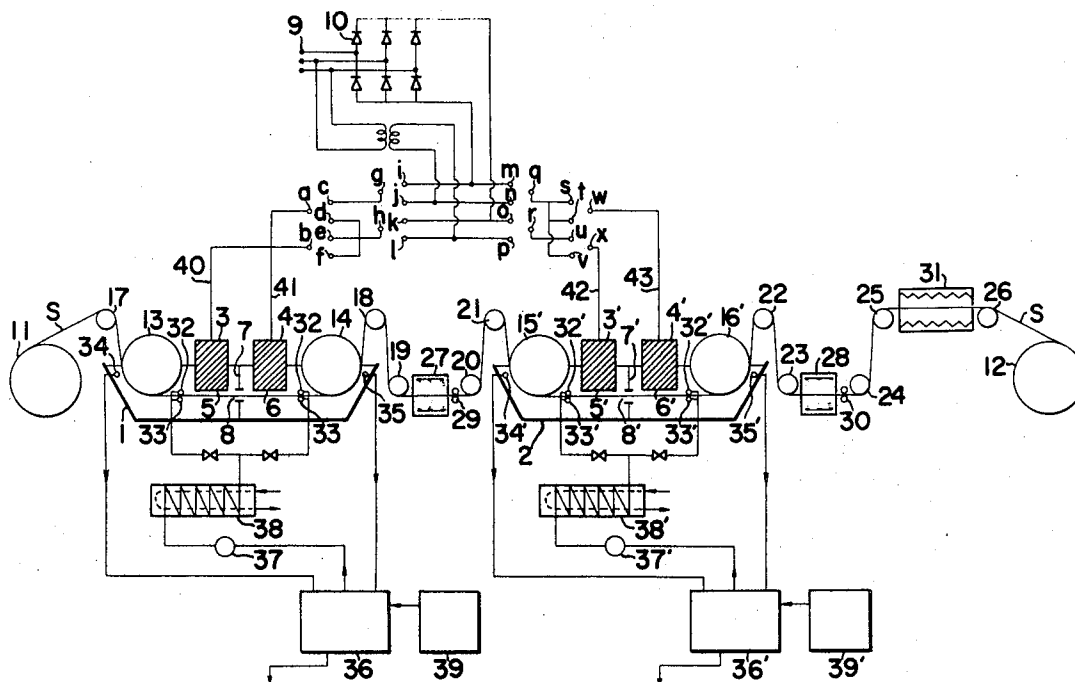
19 Claims, 2 Drawing Figures

FIG. 1

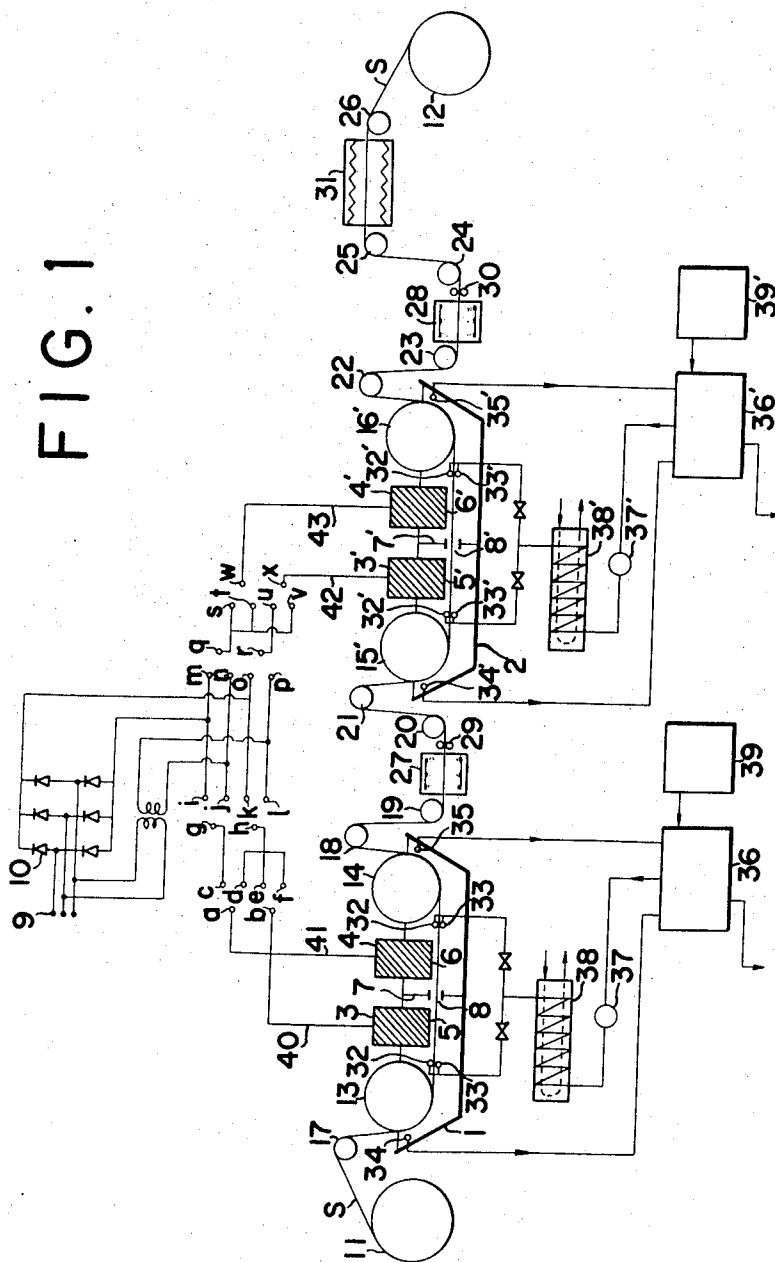
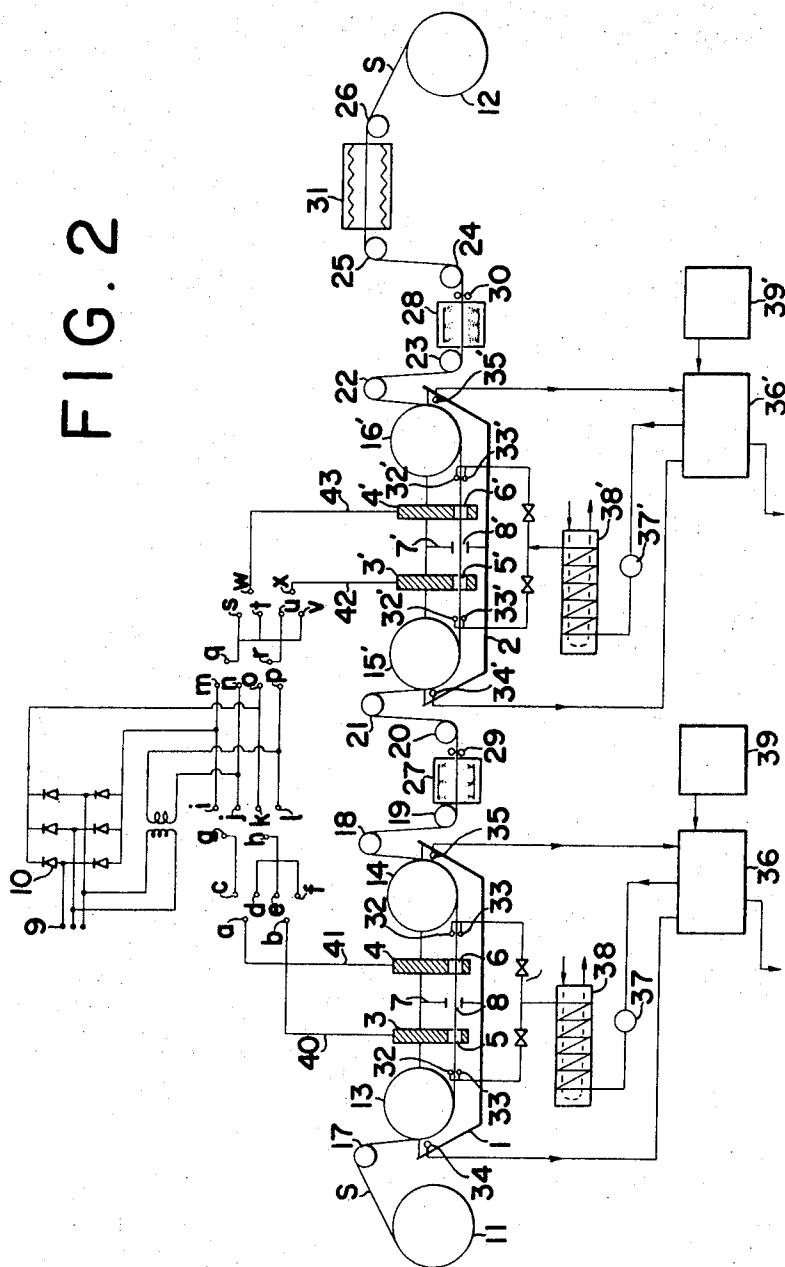


FIG. 2



PROCESS FOR THE PRODUCTION OF ALUMINUM BASE OFFSET PRINTING PLATES

This invention relates to a process for the production of aluminum base offset printing plates.

To produce an aluminum base offset printing plate from a sheet of aluminum or an aluminum base alloy, it is essentially necessary to roughen at least one surface of the aluminum sheet so as to impart thereto such properties as a good anchorage for the light-sensitive coating to be applied thereon and a good retention of water. This step of roughening the surface of the aluminum sheet may also be termed as a graining step or treatment and is one of the essential steps for the manufacture of the offset printing plates. This roughening or graining step is one procedure which necessitates always a large care and skillfulness of operator. Usually the roughening or graining process may be performed either mechanically, or chemically, or electrochemically. The mechanical graining process for the manufacture of the offset printing plates may include a ball-graining method (that is, a blast-graining method) and a brush-graining method. In the ball-graining method, however, a great care and skillfulness of operator are needed to make the selection of natures and materials for the balls and abrasive employed as well as adjustment of the moisture content in the abrasive material and control of the other many operating conditions. Besides, it is impossible to operate the ball-graining method in a continuous manner, and it is necessary to work up the aluminum sheet batch-wise from one to another. Usually the ball-graining method takes a relatively long time of e.g. 20 - 40 minutes to finish up one aluminum sheet. Accordingly this method is very much inefficient and expensive. Noticeable increase in personal expenditure which has occurred in recent years also renders the ball-graining method more inattentive from the view-point of economic.

The brush-graining method is a modification of the abrasive process which has been exploited to eliminate or minimize the above-mentioned disadvantages of the prior ball-graining method. With this brush-graining method, it is possible to perform the abrasive treatment continuously at any rate on the surface of the aluminum sheet. It is true, however, that this brush-graining method is one of the mechanical abrasive methods, and hence this method also can suffer from such disadvantages that a great care and skillfulness of operator is necessitated, for example, to make adjustment of a brush-graining machine employed and that a very much poor throughput of at most 2 m/min. or thereabout of the roughened aluminum sheet is involved. Besides, the grained surfaces of the aluminum sheets which have been roughened by means of the brush-graining method is not very satisfactory.

In order that the roughened aluminum sheets may be a material suitable for use in the manufacture of offset printing plates, it is usually necessary that the roughened surfaces of the aluminum sheet should show an average grain roughness of up to 1.5 microns, preferably of less than 1 micron and more preferably of 0.7 microns or thereabout and at least in a range of 0.7 - 1.0 microns.

As a rule, however, such aluminum base offset printing plates as manufactured from the roughened aluminum sheets which have been processed by means of the ball-graining method show the surface grains at an av-

erage grain roughness of, for example, 1.05 - 1.15 microns, and they can suffer from such drawbacks that an accurate imagewise reproduction of dots in the printed copies is difficult to be obtained from such offset printing plates, and thus the printed copies obtained are of a poor accuracy. On the other hand, such aluminum base offset printing plates as manufactured from the aluminum sheets which have been roughened using the brush-graining method usually show a low average grain roughness of e.g. 0.30 - 0.35 microns, and hence they can disadvantageously have a poor anchorage for the light-sensitive layer to such an extent that the light-sensitive layer is likely to be flaked off.

It has also been proposed to roughen the surface of aluminum base sheets by treating them electrolytically with alternating electric current in a hydrochloric acid electrolyte. However, this electrochemical method with alternating electric current in the hydrochloric acid electrolyte can suffer from such drawbacks that the grain structure given by this method is not uniform and the grained surface obtained is darkened in color owing to the deposition of aluminum smutt which has been produced during the etching operation and which is very much difficult to remove therefrom. The deposited aluminum smutt which remains on the grained surface of the offset printing plates can adversely affect on the printing performance of the plates in many ways. Besides, the grained aluminum sheet which exhibits a darkened appearance owing to the deposited aluminum smutt is not suitable as a material for the manufacture of offset printing plates, from another ground that an offset printing plate made of such a grained aluminum sheet which is contaminated by the dark deposited aluminum smutt is dark or black in color at the printing surface thereof, making it difficult for the printing worker to notice the difference between the inked-up image parts and the non-image parts of the printing surface and to find out any further contamination which might occur on the printing surface.

An object of the present invention is to provide an improved process of roughening the surface of sheets of aluminum or aluminum base alloys which is free from the above-mentioned drawbacks of the prior art roughening methods and which comprises a new electrochemically roughening treatment of treating the surface electrolytically with alternating electric current at a high current density in a modified hydrochloric acid electrolyte so that extremely fine and uniform grains having an average grain roughness of an order of 0.5 - 1.0 microns may be impart to the surface in a shorter treatment time and by which treatment there is produced a material suitable for use in the manufacture of aluminum base offset printing plates. Further object of the present invention is to provide an improved process of producing aluminum base offset printing plates comprising the new electrochemically roughening treatment as mentioned above which may be performed either batch-wise or in a continuous manner. This new electrochemically roughening treatment comprises such an electrolytical process of etching uniformly the surface of aluminum sheets in an improved aqueous electrolyte which contains hydrochloric acid as a primary etching agent and occasionally also magnesium chloride, aluminum chloride, zinc chloride and/or ammonium chloride as a secondary etching agent and which further contains essentially one or more of special amines, aldehydes, amides, urea, chromic acid and

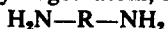
a non-ionic surface-active agent as anti-corrosive agent, so as to give fine and uniform grain structure to the surface of the sheet.

As a result of our extensive research, we have now found that when the surface of a sheet of aluminum or aluminum alloy is roughened by etching it in an aqueous hydrochloric acid electrolyte by means of alternating electric current for the purpose of producing an offset printing plate from the aluminum base sheet, better results may be obtained by carrying out the electrolytic treatment in such a hydrochloric acid electrolyte which has been modified by the addition of a total concentration of at least one of such mono-amines, di-amines and aldehydes, amides as described later, urea, chromic acid and non-ionic surface-active agents as the anti-corrosive agent.

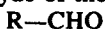
According to a generic aspect of the present invention, therefore, there is provided a process of producing an aluminum base offset printing plate, which comprises a step of roughening the surface of an aluminum base sheet by electrolytically treating it with an alternating electric current at a current density of 10 – 80 A/dm² in an electrolyte consisting of an aqueous solution containing 1 – 3 percent by weight of hydrochloric acid (calculated as HCl) and a total concentration of 0.05 percent – 5 percent (by weight based on the entire weight of said aqueous solution) of at least one anti-corrosive agent selected from a mono-amine of the formula:



wherein (i) R_1 , R_2 and R_3 are each an alkyl group of one to six carbon atoms, or (ii) R_1 and R_2 are each an alkyl group of one to six carbon atoms but R_3 is a hydrogen atom, or (iii) R_1 is an alkyl group of one to six carbon atoms, $-\text{COOH}$ or $-\text{OH}$, but R_2 and R_3 are each a hydrogen atom, or (iv) R_1 , R_2 and R_3 are each a hydroxyethyl group $-\text{C}_2\text{H}_4\text{OH}$, or (v) R_1 and R_2 are each a group $-\text{C}_2\text{H}_4\text{OH}$ and R_3 is a hydrogen atom, or (vi) R_1 is a group $-\text{C}_2\text{H}_4\text{OH}$ but R_2 and R_3 are each a hydrogen atom; a di-amine of the formula:



wherein R is an alkylene group of the formula $-\text{C}_n\text{H}_{2n}$ — and n is a whole number of 1 to 6; an aliphatic aldehyde of the formula:



wherein R is a hydrogen atom or an alkyl group of one to six carbon atoms; an amide of the formula:



wherein R is a hydrogen atom or an alkyl group of one to three carbon atoms; urea, chromic acid and non-ionic surface-active agents.

To the aqueous solution comprising hydrochloric acid as the primary etching agent which forms the aqueous electrolyte employed according to the process of the present invention, there may be incorporated, if desired, as a secondary etching agent one or more of magnesium chloride, aluminum chloride, zinc chloride and ammonium chloride to a total concentration of the chloride ions of up to 8 percent by weight of the entire weight of said aqueous solution. Thus, the electrolyte which is employed according to the present invention may be prepared by admixing either an aqueous solu-

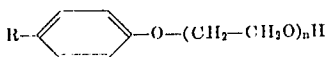
tion of 1 – 3 by weight of hydrochloric acid (as HCl) or an aqueous solution containing 1 – 3 percent by weight of hydrochloric acid (as HCl) and additionally at least one of magnesium chloride, aluminum chloride, zinc chloride and ammonium chloride at a total concentration of the chloride ions of at most 8% by weight of said aqueous solution, with proper amount(s) of one or more of the above-mentioned mono-amine, di-amine, aliphatic aldehyde, amide, urea and chromic acid.

The mono-amine of the formula $\text{NR}_1\text{R}_2\text{R}_3$ where (i) R_1 , R_2 and R_3 are each an alkyl group of one to six carbon atoms and which may be used as the anti-corrosive agent in accordance with the present invention includes trimethylamine, triethylamine, tripropylamine, tributylamines, triethylamine, trihexylamine and dimethylethylamine. The mono-amine of the above formula in which (ii) R_1 and R_2 are each an alkyl group of one to six carbon atoms and R_3 is hydrogen and which is used as the anti-corrosive agent in the present invention includes dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine and dihexylamine and the like. The mono-amine of the above formula in which (iii) R_1 is an alkyl of one to six carbon atoms, carboxyl, or hydroxyl but R_2 and R_3 are each hydrogen includes methylamine, propylamine, butylamine, pentylamine, hexylamine, carbamic acid and hydroxylamine hydrochloride etc. The mono-amine of the above formula but in which (iv) R_1 , R_2 and R_3 are each $-\text{C}_2\text{H}_4\text{OH}$ is tri-ethanol amine. The mono-amine of the above formula but in which (v) R_1 and R_2 are each $-\text{C}_2\text{H}_4\text{OH}$ but R_3 is hydrogen corresponds to di-ethanol amine. The mono-amine of the above formula but in which (vi) R_1 is $-\text{C}_2\text{H}_4\text{OH}$ but R_2 and R_3 are each hydrogen is mono-ethanol amine. The di-amine of the formula $\text{H}_2\text{N}-\text{R}-\text{NH}_2$ in which R is C_nH_{2n} and n is an integer of 1–6 includes methylenediamine, ethylenediamine, trimethylenediamine, tetramethylenediamine pentamethylenediamine and hexamethylenediamine etc.

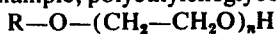
The aliphatic aldehyde of the formula $\text{R}-\text{CHO}$ in which R is an alkyl of one to six carbon atoms or a hydrogen atom includes formaldehyde (formaline), acetaldehyde and n-hexylaldehyde etc. The amide of the formula $\text{R}-\text{CONH}_2$ in which R is an alkyl group of one to three carbon atoms or a hydrogen atom includes formamide, acetamide and butylamide etc.

The aqueous electrolyte in which the aluminum base sheet is immersed and etched for the purpose of grain-ing the surface thereof may preferably contain as the anti-corrosive agent one or more of chromic acid, urea, trimethylamine, dihexylamine, trihexylamine, methylamine, n-hexylamine, methylethylamine, carbamic acid, hydroxylamine hydrochloride, tri-ethanol amine, di-ethanol amine, mono-ethanol amine, methylenediamine, hexamethylenediamine, formaldehyde, n-hexylaldehyde, formamide and butylamide.

In addition to or in place of the above-mentioned anti-corrosive agents, the aqueous electrolyte which is used in the present process may contain one or more of known non-ionic surface-active agents at a total concentration of 0.05 percent to 1 percent by weight of the anti-corrosive agent(s). As the known non-ionic surface-active agent may be used aromatic ether type one, for example, a polyethyleneglycol alkylphenyl ether of the formula:



wherein R is an alkyl group and n is a whole number, such as polyethyleneglycol octylphenyl ether, polyethyleneglycol nonylphenyl ether and polyethyleneglycol dodecylphenyl ether; higher alcohol type one, for example, polyethyleneglycol alkyl ether of the formula:



wherein R is an alkyl group and n is a whole number, such as polyethyleneglycol laurylether and polyethyleneglycol oleylether; and fatty acid derivative type one, for example, fatty acid ester of polyethyleneglycol of the formula:



wherein R is an alkyl group and n is a whole number, such as polyethyleneglycol oleate, polyethyleneglycol monostearate, polyethyleneglycol di-stearate and polyethyleneglycol monolaurate etc. A polyethyleneglycol octylphenyl ether of a molecular weight range of 300 - 1,000 is most preferred as the non-ionic surface-active agent.

Before the aluminum base sheet which may be made of purely aluminum or an aluminum alloy, for example, aluminum-magnesium alloy is treated electrolytically in the electrolyte according to the process of the present invention, it is preferred that the surfaces of the aluminum base sheet should be de-greased and cleaned by washing with a suitable organic solvent, for example, trichloroethylene, in case the surfaces of the plates have been strongly contaminated by oils and greases, particularly the rolling oils. It is also desirable that the aluminum base sheet is pre-treated in an acid pickling bath such as aqueous nitric acid and/or hydrofluoric acid to remove the oxide film which has been formed on the sheet surfaces during the rolling process.

In carrying out the process of the present invention, the aluminum base sheet is immersed in a bath of the modified electrolyte of the above-mentioned particular composition and undergoes the electrolytic treatment with alternating electric current at a high current density of 10 - 80 amperes per dm^2 while it is kept immersed within the electrolyte bath. After the graining treatment has been achieved, the grained aluminum sheet is removed out of the electrolyte bath. If the concentration of hydrochloric acid in the electrolyte employed is substantially less than 1 percent by weight, the electrolytic etching power is too weak to impart a desired roughened or grained surface to the aluminum base sheet. On the other hand, if said concentration of hydrochloric acid is substantially more than 3 percent by weight in the electrolyte, the etching can take place too strongly, involving a dissolution of the surface layer and darkening the surface of the aluminum sheet to an undesired extent, so that the desired roughened or grained surface cannot be formed.

One or more of magnesium chloride, aluminum chloride, zinc chloride and ammonium chloride may optionally be present in the electrolyte, provided that the total concentration of the chloride ions derived from these metal chloride and hydrochloric acid does not exceed 8 percent by weight of the electrolyte. These metal chlorides can act as the etching agent and also serve to increase the electric conductivity of the electrolyte and to impart a uniform grain structure to the surface of the aluminum plate. Accordingly, addition of

one or more of these metal chloride leads to a decrease in the required voltage of the electrolytic current and also in a reduction of time which is required to complete the electrolytic treatment. When one or more of magnesium chloride, aluminum chloride, zinc chloride and aluminum chloride are added to an aqueous solution of 1 - 3 percent by weight of hydrochloric acid to prepare the electrolyte to be used in the present process, it is required that the total concentration of the chloride ions should be no more than 8 percent by weight of the electrolyte as prepared. Only below this upper limit of the total chloride ion concentration, a uniform grain structure of an average grain roughness of 0.5 - 1.0 microns can be imparted to the surfaces of the aluminum sheet. In case the total chloride ion concentration increased beyond the upper limit of 8 percent by weight, the corrosion can take place severely, giving an uneven grain structure in the roughened surface of the aluminum sheet. Although it is true that the aluminum base sheet may be roughened or grained at the surfaces thereof also by performing the electrolytic treatment in an aqueous solution of aluminum chloride or in an aqueous solution of ammonium chloride, in this case it usually takes a relatively longer time of 1 - 3 minutes for the electrolytic treatment, as long as a uniform grain structure of an average grain roughness of 0.5 - 1.0 microns should be imparted to the surface of the aluminum sheet. In contrast to this, when the modified electrolyte of the above-mentioned particular composition comprising hydrochloric acid and the selected anti-corrosive agent is employed in accordance with the present invention, it normally takes only a shorter time of 20 - 60 seconds for the electrolytic treatment of one aluminum plate with the alternating electric current, with insuring that a clear, fine and uniform grained structure is imparted to the surfaces of the aluminum plate. Accordingly, the process of the present invention is of a very much improved efficiency.

The process of the present invention is characterised in that one or more of the particular mono-amines, diamines, aldehydes, amides, urea, chromic acid and non-ionic surface-active agents has been incorporated as the anti-corrosive agent at a selected total concentration into the composition of the electrolyte comprising hydrochloric acid in which the electrolytic treatment of the aluminum base sheet is effected with an alternating electric current. The anti-corrosive agent incorporated serves to control the strong etching effect of the chloride ions present, thus to ensure a fine and uniform grain structure to be imparted to the surfaces of the aluminum sheet, and further to prevent the deposition of aluminum smutt which otherwise would be deposited tenaciously on the bottom of the roughened surface of the sheet as it is produced during the etching process. In case the above-mentioned anti-corrosive agent is not incorporated into the electrolyte employed, the surfaces of the aluminum base sheet can severely be etched by the action of the chloride ions, and at the same time the insoluble smutt of aluminum which is produced owing to the etching reaction during the electrolytic treatment of the plate can remain and deposit between the grain particles on the bottom of the roughened surface so that the roughened surface of the aluminum sheet can be darkened in appearance. The addition of the anti-corrosive agent is essential and effective to prevent the darkening of the aluminum sur-

face. The anti-corrosive agent is selected from the aforesaid amines, aldehydes, amides, urea, chromic acid and the non-ionic surface-active agents, and one or more of them should be added at a total concentration of 0.05 percent or more based on the weight of the whole composition of the electrolyte. The anti-corrosive agent does not display the effect of inhibiting the darkening of the aluminum surface, however, if it is added only at a total concentration of less than 0.05 percent by weight based on the whole composition of the electrolyte. Except chromic acid, all the compounds which are available as the anti-corrosive agent in accordance with the present invention are organic compounds and contain oxygen atom or nitrogen atom which possesses a pair of non-covalent electrons. We have assumed that such oxygen atom or nitrogen atom is adsorbed on the aluminum surface to control the cathodic reaction and anodic reaction which are effected during the electrolytic process, whereby a uniformly etched graining surface can be given to the aluminum sheet in accordance with the present invention, though the present invention is not limited to this assumption. With the chromic acid, it is assumed that a passive film is formed on the aluminum surface to make moderate the etching action of the chloride ions.

The nature of the anti-corrosive agent employed may properly be chosen depending on the concentration of hydrochloric acid in the electrolyte as well as other considerations. For instance, when the electrolyte contains only hydrochloric acid as the etching agent, any of the aforesaid anti-corrosive agent are effective and satisfactory for an aqueous solution of 1 percent by weight of hydrochloric acid. However, it is found that several of the above-mentioned anti-corrosive agent, for example hydroxylamine exhibits a smaller anti-corrosive effect in an aqueous solution of 2 percent by weight of hydrochloric acid. The anti-corrosive effect of chromic acid is also decreased in an aqueous solution of 3 percent by weight of hydrochloric acid, so that its effect of preventing the darkening of the aluminum surface is reduced, too.

The current density of the alternating electric current which is employed for the electrolytic treatment in the process of the present invention may be 10 - 80 amperes per dm^2 . In case the current density employed is higher than 80 A/dm^2 , the etching is excessive, the average grain size of the roughened aluminum surface is too high and the roughness of the grained surface is not uniform. On the contrary, if the current density employed is lower than 10 A/dm^2 , the time required for the electrolytic treatment is too long and the efficiency of the treatment is reduced. When a current density of 10 - 80 A/dm^2 is employed in the process of the present invention, a higher uniformness may be obtained in the roughened aluminum surface by carrying out the electrolytic treatment for a shorter time at a higher current density, provided that a product of the current density by the duration of the electrolytic treatment is kept constant. It is most preferred that the electric density employed is in the range of 40 - 70 A/dm^2 . The alternating electric current employed may preferably be of 15 - 75 cycles per second and at 10 - 20 volts, as usual. The temperature in the electrolyte during the electrolytic treatment may suitably be in a range of 20° - 30°C. When the electrolytic treatment is carried out at a temperature of lower than 10°C or of higher than 40°C,

care is to be taken to avoid that pitting would take place at the surface of the aluminum plate.

In the process of the present invention, the electric current is employed in the form of alternating electric current for the electrolytic treatment, so that the etching can proceed moderately and smoothly to give a uniformly grained surface of the aluminum plate. If a direct electric current is employed instead of or in addition to the alternating electric current for the electrolytic treatment of the aluminum surface, it is likely that the etching would take place violently, so that the formation of a finely and uniformly grained surface would be difficult.

After the aluminum base sheet is roughened by the electrolytic etching treatment of the present invention, the sheet is then worked up in a usually manner, for example, by rinsing with water and drying. By applying thereon a known light-sensitive composition comprising a polyvinyl alcohol and the white of egg or another known light-sensitive composition comprising a light-sensitive diazo-resin, the aluminum sheet so treated is photosensitized in a known manner. This photosensitized aluminum sheet is then imagewise exposed and then developed in any convenient known way to produce an offset printing plate.

The present invention or the aluminum base offset printing plates as produced by the process of the present invention have the following advantageous characteristics:

1. The aluminum base offset printing plates as produced by the process of the present invention have very much higher uniformness in the surface roughness or the size of the surface grains, as compared to such aluminum base offset printing plates which are produced by the prior mechanical abrasive methods such as ball-graining and brush-graining. This means also a remarkable improvement in the uniformity of the retention of water over the whole surface of the aluminum base offset printing plates as produced by the process of the present invention, ensuring that the image parts of the offset printing plates may be inked up very much accurately also in minute details thereof, and that the minute details of the image parts can be reproduced with a high accuracy by means of the offset printing plates which are produced by the process of the present invention.

2. The process of the present invention permits the electrolytic etching treatment to be carried out at a high electric density and hence in a considerably reduced time of the electrolytic treatment, so that the present process is of a high productivity.

3. The process of the present invention is easily controllable, because the treatment of roughening the aluminum surface is performed electrochemically and hence may readily be carried out under such electrolytic conditions which are controlled to be steady with respect to the composition of the electrolyte, temperature, electric current density and time etc., for example. In accordance with the process of the present invention, therefore, variation in the properties of the products is little and aluminum base offset printing plates of uniform quality may be obtained without difficulty.

4. When the aluminum base offset printing plates are produced according to the mechanical abrasive methods, the products obtained from these prior art methods always would have the finished surface darkened to

a black or nearly blackish grey color. Owing to this blackish color in the surface of the prior aluminum base offset printing plates, it is difficult for the printing-operator to notice the difference between the inked-up image parts and the non-image parts of the printing surface when the printing operation is carried out in practice. With the prior aluminum base offset printing plates, therefore, it needs a large care and skillfulness to find out any contamination which might be present on the printing surface. In contrast to this, the aluminum base offset printing plates which are produced by the process of the present invention have a white or nearly white tone in the printing surface thereof, and it is easy for the workers to notice the difference between the inked-up image parts and the non-image parts of the printing surface and to find out any contamination which may exist on the printing surface.

The surfaces of the aluminum sheet which has been roughened by the alternating electric current electrolytic treatment of the present invention have a finely and uniformly grained structure which is satisfactory with respect to the fineness and uniformity of the surface grains to produce therefrom an aluminum base offset printing plates. Nevertheless, the roughened surfaces of the aluminum sheet may further be treated to gain much more improved printing characteristics. For this purpose, the process of the present invention may optionally be followed by a further step of anodizing the grained surface of the aluminum sheet and, if desired, a more further step of causing finely divided silica particles to be adsorbed by the anodized, grained surface of the aluminum sheet.

Although the aluminum sheet which has been roughened by the electrolytic graining treatment of the present invention exhibits excellent characteristics as a base material for the manufacture of aluminum base offset printing plates, its printing characteristics may further be improved as described below. Thus, when an offset printing process is performed, water is fed to over the whole printing surface of the plate in such a manner that water may be adsorbed only by the hydrophilic non-image parts of the printing surface while the greasy printing ink is inked up only in the image parts with being repelled from the oleophobic non-image parts of the printing surface. In some occasions, however, the printing ink cannot perfectly be repelled from the non-image parts during an inking-up step of a continuous offset printing process. Owing to this, it is frequent that the printing surface is gradually contaminated usually after more than 20,000 copies are obtained from one printing plate, resulting in that copies which are reproduced in the earlier phase of the printing process have clear and definite contour, while copies which are obtained in the later phase of the printing process becomes hazy in their outlines. In order to prevent the printing surface from the contamination due to the un-wanted inking up of the non-image parts and to maintain a perfect reproduction of copies of definite contour and uniform quality, it is necessary that the roughened surface of the aluminum sheet should be provided with an anodized oxide film or coating which may be formed by carrying out an anodizing treatment subsequently to the alternating electric current graining treatment of the present invention. With the aluminum offset printing plate in which the anodized oxide film has been formed, the hydrophilic nature of the non-image parts of the printing surface has been en-

hanced so that the applied ink can perfectly be repelled off from the water-carrying non-image parts, eliminating a fear that the non-image part of the printing surface would un-wantedly be inked up and contaminated. The anodized oxide film which shows a higher capacity of retention of water, as be well known, serves to prevent the "toning" or "scumming" phenomenon that the printing ink would gradually accumulate also in the non-image part of the printing surface owing to the hydrophobic nature of the other areas of the printing surface. At the same time, the anodized oxide film serves to provide the printing surface with a resistance to corrosion and abrasion as well as an improved anchorage for the light-sensitive coating to be applied.

The subsequent step of anodizing the roughened surface of the aluminum sheet may be carried out in a known manner. Thus, for instance, the oxide film may be provided over the roughened surface of the aluminum sheet by anodically oxidizing the roughened surface of the aluminum sheet with an alternating electric current or a direct electric current or a combination thereof at a current density of 1 - 20 A/dm² for a time of 20 seconds to 3 minutes in an electrolyte consisting of an aqueous solution of 15 percent by weight of sulfuric acid at an electrolyte temperature of 20°- 30°C. The oxide film which has been formed through the anodizing step may have a such thickness just sufficient to coat evenly the roughened surface of the base sheet. In practice, however, it is usually necessary that the anodized oxide film having a thickness of at least 0.1 μ should be formed to coat evenly the roughened surface of the aluminum sheet. Nevertheless, it is not desirable that the thickness of the anodized oxide film would exceed 5 μ , because the minute protruding portions of the grains at the roughened surface of the aluminum sheet would then be embedded in the too thick oxide film, resulting in an un-wantedly large reduction of the roughness of the roughened aluminum surface. A most preferred thickness of the anodized oxide film is in a range of 0.1 to 2.0 μ .

When a printing process is continued by means of an aluminum base offset printing plate set up in an offset printing machine to such an extent as to reproduce several ten thousands of copies therefrom, it is sometimes observed that the light-sensitive coating can partly be flaked off from the printing surface of the plate during the printing process so that further reproduction of the image cannot be performed. In order to prevent this trouble, it is necessary to improve further the anchorage to the light-sensitive coating and the service-life or stability of the printing surface of the plate. To this end, it has been found suitable to cause finely divided silica particles to be deposited on and adsorbed by the anodized oxide film which has been formed on the roughened surface of the aluminum sheet. The deposition and adsorption of the SiO₂ particles on and by the roughened aluminum surface may be effected in a known manner, for example, by immersing merely the roughened and anodized aluminum sheet in a dispersion of finely divided silica particles in water; or alternatively by passing a direct electric current through a bath of a dispersion in water of the finely divided silica particles which has contained the roughened and anodized aluminum sheet immersed therein, to cause the silica particles to migrate and penetrate into the anodized film of the aluminum surface by the principle of electrophoresis.

The process according to the above-mentioned generic aspect of the present invention is suitable to be carried out in a batch-wise manner by immersing an aluminum sheet in the bath of the modified aqueous electrolyte as specified in the above, effecting the electrolytic roughening treatment for the aluminum sheet which is immersed and held in the bath, and then removing the roughened or grained aluminum sheet from the bath after the completion of the roughening treatment. However, we have found that the process according to the generic aspect of the present invention produces sometimes a roughened aluminum sheet of a darkened appearance at the grained surface thereof in case the process has been worked out in a continuous manner by feeding the aluminum sheet in the form of a continuous strip or web form from the coil, continuously passing the aluminum strip into and through the electrolyte bath in the submerged condition, electrolytically roughening the surface of the aluminum strip during its continuous passage through the electrolyte bath and withdrawing continuously the roughened aluminum strip from the electrolyte bath. We have made our further research in an attempt to modify the generic aspect process of the present invention so that it can surely give satisfactory results even when it is carried out in the continuous manner to roughen the aluminum strip. We have now found that the process of the present invention may successfully be carried out in a continuous manner to roughen the continuous aluminum strip or web with giving necessarily satisfactory results when an aqueous electrolyte which essentially contains 2 - 3 percent by weight of hydrogen chloride and 0.05 - 0.5 percent by weight of a non-ionic surface-active agent selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol and which may optionally contain a mono-amine selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine is employed for the etching electrolyte and when the electrolytically roughening treatment of the aluminum strip is performed with an alternating electric current at a current density of 40 - 80 A/dm² for a residence time of 15 - 60 seconds for the aluminum strip while the aluminum strip is continuously fed into, advanced through and withdrawn from an elongated electrolysis vessel of such a particular arrangement or construction as described later.

According to a preferred embodiment of the present invention, therefore, there is provided a process for the continuous production of an aluminum base offset printing plate, which comprises a step of roughening the surface of an aluminum base sheet in the form of a continuous strip in a continuous manner by electrolytically treating the aluminum strip with an alternating electric current at a current density of 40 - 80 A/dm² for a time of 15 - 60 seconds in an electrolyte essentially consisting of an aqueous solution containing 2 - 3 percent by weight of hydrogen chloride, 0.05 - 0.5 percent by weight of a non-ionic surface-active agent which may preferably be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, up to 5 percent by weight of a mono-amine of the formula



as defined in the above which may preferably be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, and up to 5 percent by weight of a secondary etching agent selected from aluminum chloride and magnesium chloride, while advancing the aluminum strip continuously through the bath of said electrolyte in an elongated electrolysis vessel containing the electrolyte bath in the cavity thereof, wherein the cavity of the electrolysis vessel is substantially divided into two sections by an intermediate vertical wall which locates substantially at the middle of the longitudinal axis of the vessel, which extends across the whole width of the vessel and which contains a communicating orifice adapted to insure that the aluminum strip is freely passed through said orifice with keeping the aluminum strip submerged in the electrolyte bath and that the electrolyte is allowed to freely flow through said orifice to make a communication between the above-mentioned two sections of the vessel cavity, and wherein each of these two sections of the vessel cavity contains therein at least one electrode of which one surface is faced to and spaced from the surface of the advancing aluminum strip to be roughened.

The process according to the preferred embodiment of the present invention may advantageously be effected in the following ways (A) to (E).

A. The aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 - 80 A/dm² for a time of 15 - 60 seconds in an aqueous electrolyte containing 2 - 3 percent by weight of hydrogen chloride and 0.05 - 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such arrangement as described in the above.

B. The aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 - 80 A/dm² for a time of 15 - 60 seconds in an aqueous electrolyte containing 2 - 3 percent by weight of hydrogen chloride, 0.05 - 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, and up to 5 percent by weight of aluminum chloride or magnesium chloride, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such arrangement as described in the above.

C. The aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 - 80 A/dm² for a time of 15 - 60 seconds in an aqueous electrolyte containing 2 - 3 percent by weight of hydrogen chloride, 0.05 - 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, and 0.05 - 5 percent by weight of a mono-amine which may be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, while advancing the alu-

minum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such an arrangement as described in the above.

D. The aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, 0.05 – 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, 0.05 – 5 percent by weight of a mono-amine which may be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, and up to 5 percent by weight of aluminum chloride or magnesium chloride, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such an arrangement as described in the above.

E. The aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 70 A/dm² for a time of 20 – 30 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, up to 3 percent by weight of aluminum chloride, 0.5 – 3 percent by weight of tri-ethanol amine and 0.05 – 0.1 percent by weight of a non-ionic surface-active agent which may preferably be polyethyleneglycol octylphenyl ether.

Plants suitable for working out the process according to the above-mentioned preferred embodiment of the present invention are now described with reference to the accompanying drawings.

In the accompanying drawings:

FIG. 1 shows diagrammatically a plant for continuously producing a roughened aluminum strip which comprises a series of two electrolysis vessels, by treating electrolytically a continuous aluminum strip in a continuous manner with an alternating electric current which is supplied from a pair of two electrodes in the form of a block suspended in the two sections of one electrolysis vessel, the aluminum strip being submerged in, passed through the electrolyte bath and advanced below the lower side of each electrode.

FIG. 2 shows diagrammatically a modification of the plant of FIG. 1 in which each of the pair of electrodes suspended in the two sections of the electrolysis vessel is fitted with a slot perforated therein through which the advancing aluminum strip may freely pass while being submerged in and passed through the electrolyte bath.

Referring to FIG. 1, the plant according to the present invention comprises a series of a first electrolytic vessel 1 and a second electrolytic vessel 2. The first and second electrolytic vessels 1 and 2 have the same arrangement or construction, and for a convenience of explanation, only the construction of the first electrolytic vessel 1 is described below. The vessel 1 is provided with two opposite electrodes 3 and 4 which may be made of a suitable material, for example, carbon or graphite. These electrodes 3 and 4 are each shaped in the form of a block of which the lower side 5 or 6 is faced to and spaced from the upper surface of the aluminum strip S to be roughened. If desired, these opposite electrodes 3 and 4 may be in the form of a flat

plate, respectively. An intermediate vertical wall 7 is interposed between the opposite electrodes 3 and 4 approximately at the middle of the longitudinal axis of the vessel to extend across the whole width of the vessel, so that the cavity of the vessel is substantially divided into two sections. This wall 7 is also machined to contain such an orifice 8 through which the aluminum strip can pass freely without contacting with the wall 7. The electrolyte is placed in the cavity of the electrolysis vessel 1 and is allowed to flow only through the orifice 8 in the wall 7 to make a communication between the two sections of the vessel cavity.

The electrolyte is led from its storage tank 36 to a pump and then into a heat-exchanger 38 for heating or cooling the electrolyte where the temperature of the electrolyte is adjusted to a pre-determined one. After leaving the heat-exchanger 38, the electrolyte is ejected into the electrolysis vessel 1 through the nozzles 32 and 33. Outlets 34 and 35 are provided at the forward and afterward ends of the vessel 1 for discharging an overflow of the electrolyte, and this overflow of the electrolyte is sent back through the outlets 34 and 35 into the storage tank 36. The storage tank 36 is supplied successively with a supplemental fresh flow of the electrolyte from an electrolyte-feeding tank 39. An aluminum strip S is un-coiled from the coil 11 and continuously fed through a guide-roll 17 into the front section of the first electrolysis vessel 1, and the aluminum strip S passes through the front and rear sections of the vessel cavity by advancing successively below the lower side 5 of the electrode 3, through the orifice 8 in the wall 7 and then below the lower side 6 of the electrode 4 while it is submerged within the electrolyte bath present in the first electrolysis vessel 1. During this passage, it is supported and guided by the strip-supporting rollers 13 and 14 without contacting with the bodies of the electrodes and the intermediate wall. The aluminum strip S is then continuously withdrawn from the rear section of the first vessel 1. The first electrolysis vessel 1 is filled with the electrolyte of the above-mentioned especial composition comprising hydrochloric acid as a primary etching agent and one or more of the above-mentioned anti-corrosive agents added to the particular concentration(s).

To supply an appropriate alternating electric current to the opposite electrodes 3 and 4 in the first electrolysis vessel 1 and to supply an appropriate alternating or direct electric current or a combination thereof to the opposite electrodes 3' and 4' in the second electrolysis vessel 2, there is arranged a distribution network which comprises bus bars 9 for carrying a three-phase alternating electric current, rectifiers, a transformer and switching terminals c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u and v. By effecting appropriate electrical connections between these terminals c to v and terminals a and b and terminals w and x in a convenient manner as illustrated in Examples 6 – 18 later, an appropriate alternating electric current may be fed at a suitable intensity to the opposite electrodes of the first electrolysis vessel 1, while an appropriate alternating or direct electric current or a combination thereof may be fed at a suitable intensity to the opposite electrodes of the second electrolysis vessel 2. Thus, by arranging that the terminals a and b of the leads 40 and 40' for the electrodes 3 and 4 provided in the first electrolysis vessel 1 are electrically connected with any suitable two of the switching terminals c, d, e and f which, in turn, have

been connected through the terminals *g* and *h* with any suitable two of the terminals *i*, *j*, *k* and *l* of the aforesaid distribution network, an alternating electric current is supplied to the pair of the electrodes 3 and 4 in the first vessel 1 to pass through the electrolyte bath which fills the cavity of the first vessel and within which the aluminum strip *S* advances continuously. In this situation, the electrolytic process takes place at the surface of the running aluminum strip *S* so as to roughen or gain the aluminum surfaces.

The aluminum strip *S* which has been roughed at the surface thereof in the first electrolysis vessel 1 is then passed around guide-rollers 18 and 19 and then into a rinsing chamber 27 in which the strip is washed by means of water spray. The aluminum strip which has left the rinsing chamber is then passed between draining rollers 29 and around guiding rollers 20 and 21 and subsequently into the second electrolysis vessel 2.

The second electrolysis vessel 2 may be filled with an anodizing electrolyte, for example, an aqueous solution of 15 percent sulfuric acid, which brings an anodic oxidation into effect at the surfaces of the aluminum strip. Terminals *w* and *x* of the leads 42 and 43 for the pair of the electrodes 3' and 4' which are provided in the second electrolysis vessel 2 are arranged to be connected with appropriate two of terminals *s*, *t*, *u*, *v* of the distribution network to supply an alternating current or a direct current to said pair of the electrodes.

While submerged in the electrolyte bath present in the second electrolysis vessel 2, the aluminum strip *S* is advanced successively below the lower side 5' of the electrode 3', through the orifice 8' in the intermediate wall 7' and then below the lower side 6' of the electrode 4' without contacting with the bodies of the electrodes 3' and 4' and the wall 7'.

In the second electrolysis vessel 2, guide rollers 15 and 16, inlets 34' and 35' and pairs of nozzles 32' and 33' operate in the same way as the corresponding members 15, 16, 34, 35, 32 and 33 which are provided in the first electrolysis vessel 1, respectively. Electrolyte storage tank 36', feed tank 39', pump 37' and heat-exchanger 38' which are provided for the second vessel 2 also operate in the same manner as the corresponding devices 36, 39, 37 and 38 for the first vessel 1, respectively. When the terminals *w* and *x* of the leads 42 and 43 for the electrodes 3' and 4' provided in the second electrolysis vessel 2 are electrically connected with any suitable two of the terminals *s* to *v* of the distribution network so that an alternating electric current is passed between the electrodes 3' and 4' through the electrolyte in the second vessel 2. In this way, the grained surfaces of the aluminum strip *S* undergo the actions of the alternating electric current and the electrolyte and is coated with the aluminum oxide film as it is formed through the anodic oxidation of the aluminum surfaces according to the known principle.

A direct electric current may be fed to the pair of the electrodes 3' and 4' in the second electrolysis vessel 2 by electrically connecting the terminal *x* of the lead 42 of the electrode 3' with a positive terminal for supply of direct electric current from said distribution network and connecting the terminal *w* of the lead 43 of the electrode 4' with the negative terminal for supply of the direct electric current from said network. The direct electric current may be prepared in the distribution network by rectifying the three-phase alternating cur-

rent from the bus bars 9 by means of the rectifier 10 in a known manner.

When the terminals *w* and *x* of the leadings 42 and 43 are connected with the positive pole and negative terminals for supply of a direct electric current, respectively, the electrode 3' forms a positive electrode. Thus, a length of the aluminum strip *S* running in the front section of the second electrolysis vessel 2 into which the aluminum strip is supplied behaves as a negative electrode. Accordingly, gaseous hydrogen is generated at the surfaces of the length of the aluminum strip which is located within the front section of the second electrolysis vessel 2, so that an electrolytic de-greasing treatment is effected at said surfaces of the aluminum strip. Since the anti-corrosive agent has been incorporated in the electrolyte which is placed in the first electrolysis vessel 1, the smutt as formed during the electrolytic etching treatment has almost completely been removed from the aluminum strip surfaces through the action of the anti-corrosive agent. Any possible trace of the smutt which would still remain on the aluminum strip can thoroughly be removed in the front section of the second electrolysis vessel 2 through the electrolytic de-greasing treatment which is effected therein, insuring a complete removal of the smutt. On the other hand, the electrode 4' forms a negative electrode in the second electrolysis vessel 2 so that a length of the aluminum strip *S* running in the rear section of the second electrolysis vessel 2 from which the aluminum strip is discharged behaves as a positive electrode. Thus, the anodizing process takes place to form the aluminum oxide layer on the grained surface of the length of the aluminum strip *S* which is running in the rear section of the second electrolysis vessel 2.

The aluminum strip *S* which has been oxidized anodically in the entire sections or in the rear section of the second electrolysis vessel 2 is then withdrawn from the vessel and passed around guide-rollers 22 and 23 and enters into a water-rinsing chamber 28 where it is washed with sprayed water. The aluminum strip which has left the rinsing chamber is passed between draining rollers 30 and then enters into a drying device 31 via guide-rollers 24 and 25. When the aluminum strip has well been dried by blowing cold air and/or hot air etc., in the drying device, it is guided by a guide-roller 26 and wound up into a coil by means of a re-coiler 12.

In accordance with another form of operating the plant of FIG. 1, an aqueous electrolyte comprising 1 - 3 percent by weight of hydrochloric acid as the primary etching agent may be placed in both the first and second electrolysis vessels 1 and 2, and the terminal *a* and *b* of the leads 40 and 41 of the electrodes 3, 4 in the first vessel as well as the terminals *w* and *x* of the leads 42 and 43 of the electrodes 3' and 4' of the second electrolysis vessel 2 may be connected to such terminals for supply of alternating electric current, respectively. In this case, the aluminum strip *S* undergoes the electrolytically etching treatment in both the vessels 1 and 2, so that the aluminum strip can then be roughened with a shorter residence time in each vessel to give the same degree of graining, as compared to such a case when the electrolytically etching treatment is effected only in the first electrolysis vessel 1 as described above. In this case, therefore, it is possible to feed the aluminum strip at a higher speed and hence to produce the roughened aluminum base sheet at a higher throughput.

In the electrolysis vessel 1 or 2 having the arrangement or construction as shown in FIG. 1, the supply of electric current to the aluminum strip S may be effected while keeping such a condition that this aluminum strip is not contacted with any of the electrodes. In contrast to this, in case supply of an electric current to the aluminum strip is effected through any contact roll which is kept in electrical contact with the surface of the aluminum strip and which is connected with a source of the electric current, it is not feasible to supply a large electric current because sparking is likely to occur due to the large electric current so that overheating of the aluminum strip is likely to take place owing to the sparking. With the electrolysis vessel of the arrangement or construction as shown in FIG. 1, the supply of an electric current to the aluminum strip may be effected via the electrolyte bath through which the aluminum strip is passing without contacting with any of the positive and negative electrodes, and it is feasible to supply a large electric current to the electrolysis vessel. Accordingly, the electrolysis vessel as shown in FIG. 1 is very much suitable for carrying out the process of the present invention according to which the electrolytically etching treatment of the aluminum sheet may be performed for a reduced treatment time using the alternating electric current at a high current density. Each of the first and second electrolysis vessels 1 and 2 are divided into the two sections by means of the intermediate vertical wall 7 containing the orifice 8 through which the aluminum sheet can freely pass and through which the electrolyte can flow to communicate between the two sections of the vessel. One electrode is suspended in each of these two sections of each vessel, so that the aluminum strip undergoes the electrolytical treatment in each section of the vessel and hence undergoes the electrolytic treatment twice in each vessel. With the electrolysis vessel of the construction as shown in FIG. 1, therefore, it is possible to increase the speed of passage of the aluminum strip which is passing through the electrolysis vessel, as compared to such a case when only one electrode is provided in one electrolysis vessel to effect the electrolytic treatment of the aluminum strip.

The temperature in the electrolyte as well as the temperature in the aluminum strip present in the electrolysis vessels tend to be raised considerably owing to the passage of the alternating electric current at a high current density. In the first and second electrolysis vessels, however, there are provided the nozzles 32, 33, 32' and 33' for ejecting fresh streams of the electrolyte which has been cooled down by means of the heat-exchangers 38 and 38'. The cooled stream of the electrolyte is constantly ejected from the nozzles 32, 33, 32' and 33' with aid of the action of the pump 37 and 37' towards the gaps formed between the aluminum strip and the lower side of the electrode. In this way, the ejected, cold stream of the electrolyte passes rapidly through said gaps formed between the upper surface of the aluminum strip and the lower face of the electrode to remove the heat from the aluminum strip and simultaneously to force the electrolyte to circulate within the electrolysis vessels. Accordingly, the temperature in the electrolyte bath is distributed evenly in each of the electrolysis vessels at all times, so that the electrolytic reactions take place also evenly in each of the electrolyte bath without involving any un-wanted local reaction. This assists in forming the uniformly grained sur-

face of the aluminum sheet and also in producing the uniform aluminum oxide layer thereon.

Referring to FIG. 2, there is diagrammatically shown a modification of the plant of FIG. 1. The plant of FIG. 2 has the same arrangement or construction as that of the plant of FIG. 1 except that each of the electrodes provided in the first and second electrolysis vessels is modified by being perforated to form a slot in the lower part of the electrode, through which slot the running aluminum strip can freely pass without coming into contact with the body of the electrode. In FIG. 2, the same reference numerals as those of FIG. 1 denote the same elements or members of the plant as those of the plant of FIG. 1, excepting that the reference numerals 5, 6, 5' and 6' given in FIG. 2 represent the slots which are provided in the electrodes 3, 4, 3' and 4', respectively, in stead of the lower sides or lower faces of the block form of the electrodes 3, 4, 3' and 4' shown in FIG. 1.

The plant of FIG. 2 operates substantially in the same manner as the plant of FIG. 1 only except that the aluminum strip which has been continuously fed into the first or second electrolysis vessel passes through the front and rear sections of each vessel by advancing successively through the slot 5 or 5' in the electrode 3 or 3', through the orifice 8 in the wall 7 and then through the slot 6 or 6' in the electrode 4 or 4' while it is submerged in the electrolyte bath present in each vessel. The lower part of each electrode is fitted with one slot perforated therein through which the advancing aluminum strip can freely pass without coming into contact with the body of the electrode, and the slots are so positioned that the slots of the two opposite electrodes and the orifice of the intermediate wall are aligned with each other in each vessel, permitting that the advancing aluminum strip passes straight horizontally through said slots and orifice while it is submerged in the electrolyte bath. During the passage of the aluminum strip through the slots in the electrodes, the electrolytically roughening treatment takes place on the upper and lower surfaces of the aluminum strip. During this passage, the electric current can be supplied to the aluminum strip at a uniform electric current density over the whole width of the aluminum strip which is passing through the slot of the electrode, so that a very much uniform graining can be achieved over the whole surfaces of the aluminum strip with simultaneously causing the edges of the aluminum strip to be etched so as to remove any sharp dentation of the said edges and thus form beveled edges of the aluminum strip.

According to a further aspect of the present invention, therefore, there is provided an apparatus for electrolytically roughening an aluminum base sheet in the form of a continuous strip, comprising an elongated electrolysis vessel containing an aqueous electrolyte and provided with an intermediate wall which locates substantially at the middle of the longitudinal axis of the vessel and extends across the whole width of the vessel to divide the cavity of the vessel into two sections and which is fitted with a communication orifice perforated therein below the level of the electrolyte bath and adapted to allow the aluminum strip to freely pass through said orifice without contacting with the material of the intermediate wall; and further provided with two electrodes which are each positioned in each section, the lower part of said electrode being fitted with a slot perforated therein, said slot being adapted to

allow the aluminum strip to freely pass without coming into contact with the body of the electrode, the slots of the two electrodes and the orifice of the intermediate wall being aligned with each other and positioned below the level of the electrolyte bath in the vessel.

Moreover, it may be added that the process according to the above-mentioned preferred embodiment of the present invention can be worked out also in a further modification of the plant of FIG. 1 wherein the first electrolysis vessel as shown in FIG. 1 has been replaced by an apparatus of such an arrangement as shown in FIGS. 3 and 4 of the accompanying drawings of U.S. Pat. No. 3,359,190 if an alternating electric current is fed to the electrodes of said apparatus, although the method of the U.S. Pat. No. 3,359,190 is directed to a continuous anodization of an aluminum strip.

The invention is now illustrated with reference to Examples, but the present invention is not limited thereto in any way.

EXAMPLE 1

Aluminum sheets which each is 0.2 mm thick and has a size of 300 mm × 400 mm are de-greased by washing with trichloroethylene rinsed then rinsed with water at room temperature. The cleaned sheets are electrolytically roughened by a treatment at room temperature under such etching conditions as indicated in Table 1 in aqueous electrolytes of various compositions as shown in Table 1, which electrolytes are each flown through by an alternating electric current having a current density as indicated in Table 1. The etching conditions employed and the average grain roughness obtained at the roughened surfaces of the aluminum sheets are shown in Table 1 below.

TABLE 1

Composition of electrolyte (percent by weight)

Experi- ment number	Primary etching agent (HCl) percent	Secondary etching agent	Water, percent	Anti-corrosive agent	Current density (A/dm. ²)	Elec- trolysis time, second	Elec- trolysis tempera- ture, ° C.	Average grain rough- ness, μ
1.....	1	-----	99	0.2% hydroxylamine hydrochloride.....	40	60	20-25	0.78
2.....	1	-----	99	0.1% chromic acid.....	20	45	20-25	0.50
3.....	2	-----	95	3% formaldehyde.....	60	60	20-25	0.81
4.....	2	-----	95	3% formamide.....	60	30	20-25	0.75
5.....	1	2% ammonium chloride.....	96	1% triethanol amine.....	20	60	20-25	0.79
6.....	2	do.....	97.94	0.06% polyethylene glycol octylphenyl ether.....	40	60	20-25	0.77
7.....	2	1% aluminum chloride.....	96.4	0.2% triethanol amine plus 0.4% urea.....	40	60	20-25	0.75
8.....	1	2% aluminum chloride plus 0.5% magnesium chloride.....	95.4	1% trihexylamine plus 0.1% polyethylene glycol lauryl ether.....	40	60	20-25	0.74
9.....	2	2% aluminum chloride plus 0.5% zinc chloride.....	94	1% monoethanol amine plus 0.5% dihexylamine.....	60	60	20-25	0.80
10.....	2	-----	97	1% n-hexylaldehyde.....	60	60	20-25	0.79
11.....	1	-----	97.9	1% butylaldehyde plus 0.1% polyethylene glycol lauryl ether.....	40	60	20-25	0.76
12.....	2	-----	95	1% hexamethylene diamine plus 2% carbamic acid.....	60	30	20-25	0.74
13.....	1	-----	96	1% trimethylamine plus 2% diethanol amine.....	40	60	20-25	0.74
14.....	2	-----	97	1% methylethylamine.....	60	60	20-25	0.78
15.....	1	-----	96	1% methyldiamine plus 2% formaldehyde.....	40	60	20-25	0.75
16.....	2	-----	95	1% n-hexylamine plus 2% formamide.....	60	60	20-25	0.79
17 (com- para- tive).	3	-----	97	-----	40	60	20-25	0.40

All the aluminum sheets treated in the experiments Nos. 1 - 16 have uniformly grained surface which shows an average grain particle roughness as indicated in the above Table and exhibits a whity colored appearance and is free from the black smutt of aluminum which would have been formed during the etching treatment. On the contrary, the aluminum sheet treated in the comparative experiment No. 17 has a roughened surface which is not uniform in the grain size and shows

a black colored appearance owing to a large amount of the black smutt which has tenaciously been deposited between the grain particles.

The electrolytically roughened aluminum sheets so obtained from the experiments Nos. 1 - 16 are subsequently rinsed with water, dried and then coated by application of a liquid preparation comprising a light-sensitive diazo-resin which is known as available for the manufacture of the "wipe-on" type offset printing plates. After drying, the photosensitized sheets are im-
agewise exposed to actinic light from a carbon arc lamp for 3 minutes under a negative pattern combined with a gray scale with dot (200 lines per inch). The aluminum sheets are then developed, rinsed with water and coated with gum arabic to give a hydrophilic surface so that the offset printing plates are thus produced.

These offset printing plates show a good reproducibility of printed dots, as the printed dots are reproduced accurately in the copies even in any minute image parts thereof. When a printing process is made with these offset printing plates, set up in an offset printing machine, 20,000 copies of perfectly uniform quality can be obtained from each plate without involving any reduction in the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

The electrolytically roughened aluminum sheet obtained from the experiment No. 21 is unsuitable to manufacture the offset printing plate owing to its blackish appearance.

EXAMPLE 2

An aluminum sheet which is 0.2 mm thick and has a size of 300 mm × 400 mm is degreased by washing with

trichloroethylene and then rinsed with water. The cleaned aluminum sheet is dipped and electrolytically roughened by a treatment in an electrolyte essentially consisting of an aqueous solution of 1 percent by weight of hydrogen chloride and 0.2 percent by weight of hydroxylamine hydrochloride through which alternating electric current is flowing at a current density of 20 A/dm². The electrolytic treatment is carried out for a time of 60 seconds and at an electrolyte temperature

of 20°C. A uniformly roughened surface of an average grain roughness of 0.78 μ is formed in the surface of the aluminum sheet. After rinsing with water, the roughened aluminum sheet is anodized by treating with a direct electric current at a current density of 2 A/dm² for 1 minute and in an electrolyte essentially consisting of an aqueous solution of 15 percent by weight of sulfuric acid at an electrolyte temperature of 30°C. An aluminum oxide layer of 0.5 μ thick is formed on the roughened surface of the aluminum sheet through this anodizing treatment. After rinsing and drying, the aluminum sheet so treated is photosensitized by coating with a liquid preparation comprising a known light-sensitive diazo resin for the wipe-on plates. After drying, the photosensitized aluminum sheet is imagewise exposed for 3 minutes to actinic light from a carbon arc lamp under a negative master combined with a gray scale with dot (200 lines per inch). The aluminum sheet is subsequently developed, rinsed with water and then made hydrophilic at the surface thereof by application of gum arabic, so that offset printing plates are produced.

A printing process is made with the offset printing plate set up in an offset printing machine. 20,000 copies of perfectly uniform quality can be obtained from this plate, and the printed dots even in the minute details of the image parts are reproduced accurately in all the copies with giving the printed image of definite contour but without involving any contamination at the printing surface of the plate.

EXAMPLE 3

An aluminum sheet which is 0.2 mm thick and has a size of 300 mm $\times$ 400 mm is degreased by washing with trichloroethylene and then rinsed with water. Thereafter, the cleaned aluminum sheet is electrolytically roughened at the surfaces thereof by treating it with alternating electric current at a current density of 40 A/dm² in an electrolyte which is an aqueous solution of 1 percent by weight of hydrogen chloride, 2 percent by weight of ammonium chloride and 1 percent by weight of triethanol amine. The electrolytic treatment is carried out for a time of 60 seconds and at an electrolyte temperature of 20°C. A uniformly roughened surface of an average grain roughness of 0.79 μ is formed at the surfaces of the aluminum sheet. After washing with water, the roughened aluminum sheet is anodized by treating with a direct electric current at a current density of 15 A/dm² in an aqueous solution of 15 percent by weight of sulfuric acid. This anodizing treatment is effected for an electrolysis time of 30 seconds and at a solution temperature of 30°C. An anodized oxide film of 0.5 μ thick is formed at the roughened surfaces of the plate. After washing with water and drying, the aluminum sheet so treated is then photosensitized by providing thereon a light-sensitive coating from a known liquid preparation comprising light-sensitive diazo resin for the wipe-on plate. The photosensitized aluminum sheet is imagewise exposed for 2 minutes to actinic light from a carbon arc lamp under a negative pattern and a gray scale with dot (200 lines per inch). The aluminum sheet is then developed, rinsed with water and further made hydrophilic at the surface thereof by application of a coating of gum arabic to produce an offset printing plate. When a printing process is made using the printing plate set up in an offset printing machine, the dots are accurately reproduced in copies

even in the minute details of the image part still after 20,000 copies have been printed from this plate. No contamination can be observed at the printing surface of the plate, and printed images of definite contour can be maintained in all the copies.

EXAMPLE 4

An aluminum sheet which is 0.2 mm thick and has a size of 400 mm $\times$ 255 mm is de-greased by washing with trichloroethylene and then rinsed with water. The cleaned aluminum sheet is then electrolytically roughened at the surface thereof by treating in an electrolyte which is an aqueous solution of 2 percent by weight of hydrochloric acid and 3 percent by weight of formamide and which electrolyte is flown through by alternating electric current at a current density of 60 A/dm². This electrolytic treatment is carried out for an electrolytic time of 30 seconds and at an electrolyte temperature of 20°C, so that a uniformly roughened surface of an average grain roughness of 0.75 μ is given to the aluminum sheet. After washing with water, the aluminum sheet is subjected to an anodizing treatment for 1 minutes in an aqueous solution of 15% by weight of sulfuric acid through which a direct electric current is passing at a current density of 2 A/dm² and which is maintained at a temperature of 30°C. In this way, an anodized oxide film of 0.5 μ thick is formed at the roughened surface of the sheet. After washing with water, the aluminum sheet with the oxide film is immersed in an aqueous colloidal dispersion of 5 percent of silica sol at room temperature for 5 minutes and then removed out from said dispersion. After heating and drying the wet aluminum sheet at 70°–80°C, it is observed that the oxide film present on the aluminum sheet contains the particles of SiO₂ adsorbed therein. The aluminum sheet so treated is then photosensitized by application of a photosensitive coating from a liquid preparation comprising a diazo resin which is known for use in the manufacture of the "wipe-on" type of offset printing plates. The photosensitized aluminum plate is imagewise exposed for 2 minutes to actinic light from a carbon arc lamp under a negative pattern and a gray scale with dot (200 lines per inch). The aluminum sheet is then developed and rinsed with water to give an offset printing plate. When the printing process is done using this plate set up in an offset printing machine, this plate shows a good anchorage for the light-sensitive coating to such an extent that the light-sensitive coating is not flaked off still after 25,000 copies are printed from this plate. The dots in the minute details of the image parts are perfectly reproduced in all the copies.

EXAMPLE 5

An aluminum sheet which has a dimension of 400 mm $\times$ 255 mm $\times$ 0.2 mm thickness is de-greased by washing with trichloroethylene and then rinsed with water. The cleaned aluminum sheet is electrolytically roughened by treating in an electrolyte which is an aqueous solution of 2 percent by weight of hydrochloric acid, 2 percent by weight of ammonium chloride and 0.1 percent by weight of polyethylene glycol octylphenyl ether and which electrolyte is flown through by alternating electric current at a current density of 40 A/dm² and at an electrolysis voltage of 5–6 V. The electrolytic treatment is then carried out for an electrolysis time of 60 seconds and at an electrolyte temperature of 20°C, so that a uniformly roughened sur-

face of an average grain roughness of $0.77\ \mu$ is formed at the surface of the aluminum sheet. After washing with water, the roughened aluminum sheet is anodized by treating in an aqueous solution of 15 percent by weight of sulfuric acid which is flown through by a direct electric current at a current density of $15\ \text{A/dm}^2$ and is kept at a temperature of 30°C . The anodizing treatment is carried out for 30 seconds, so that an oxide film of $0.5\ \mu$ thick is formed on the roughened surface of the aluminum sheet. After washing with water, the anodized aluminum sheet is immersed in an aqueous colloidal dispersion of 5 percent of silica sol, and a direct electric current is passed through this silica dispersion containing the immersed aluminum plate for 1 minute at a voltage of 60 V and at room temperature while the anodized aluminum sheet is set as a positive pole and a carbon plate as a negative pole. In this way, the disperse particles of SiO_2 are caused to migrate toward and penetrate into and well be adsorbed by the anodized oxide film of the aluminum sheet from the colloidal dispersion of silica. The aluminum sheet so treated is then dried and photosensitized by application of a light-sensitive coating from a known liquid preparation of a light-sensitive diazo resin which is usually employed in the manufacture of the wipe-on type of offset printing plates. The photosensitized aluminum sheet is subsequently processed in the same manner as in Example 4 to produce an offset printing plate.

When the printing process is carried out using the printing plate set up in an offset printing machine, this plate shows an enhanced anchorage for the light-sensitive coating as well as an improved stability of the printing surface thereof to such an extent that the light-sensitive coating is not flaked off still after 30,000 copies are printed from this plate. In addition, the printed dots are perfectly reproduced even in minute details of the image parts in all the copies obtained.

EXAMPLE 6

This example illustrates a continuous production of an offset printing plate according to the process of the present invention by means of the plant which is diagrammatically shown in FIG. 1 of the accompanying drawing.

A continuous strip S of aluminum which is 300 mm wide and 0.3 mm thick is electrolytically treated in a series of the first electrolysis vessel 1 and second electrolysis vessel 2 in the following manner.

The aluminum strip S is continuously fed into the first electrolysis vessel 1 containing an electrolyte which is an aqueous solution of 3 percent by weight of hydrogen chloride and 0.1 percent by weight of polyethyleneglycol octylphenyl ether (a non-ionic surface-active agent) in the cavity thereof. The temperature in the electrolyte is maintained at 25°C . By effecting electrical connections between the terminals g and j, between the ones h and l, between the ones a and d, and between the ones b and f, alternating electric current is supplied to the electrodes 3 and 4 of graphite so that the electrolyte is flown through by an alternating current at a current density of $60\ \text{A/dm}^2$. While submerged in the electrolyte bath, the aluminum strip S advances constantly to pass below the lower side of the electrode 3, through the orifice 8 in the intermediate wall 4 and then below the electrode 4 at such a speed that the residence time of the aluminum strip within this first electrolysis vessel is 17 seconds. The orifice 8 has such dimensions that

the advancing aluminum strip can freely pass there-through without contacting with the materials of the intermediate wall. The dimensions of the orifice 8 are such that the depth of orifice is 20 mm and that the distance between the upper boundary of the orifice and the upper side of the aluminum strip, the distance between the lower boundary of the orifice and the lower side of the aluminum strip and the distances between the two lateral sides of the aluminum strip and the lateral boundaries of the orifice are 25 mm, respectively. The electrolyte is supplemented at a total rate of 100 litres/min. from the opposite pairs of the nozzles 32 and 33.

The aluminum strip which has left the first electrolysis vessel 1 is then rinsed with water in the rinsing chamber 27 and passed between the draining roller to remove the water layer which is adhering on the roughened surface of the aluminum strip. The aluminum strip is subsequently fed into the second electrolysis vessel 2 containing an aqueous electrolyte of the same formulation as that of the electrolyte present in the first vessel 1 at a temperature of 25°C , and it is submerged and runs within the electrolyte bath to pass successively below the electrode 3', through the orifice 8' in the intermediate wall and below the electrode 4' of the second vessel 2. The arrangement and dimensions of these opposite electrodes as well as the intermediate wall 2 are the same as those of the corresponding members in the first vessel 1. By effecting electrical connections between the terminals n and q, between the ones p and r, between the ones t and w and between the ones v and x, alternating electric current is supplied to the electrodes 3' and 4' in the second vessel, so that the electrolyte is flown through by an alternating current at a current density of $60\ \text{A/dm}^2$ in the second vessel. After the aluminum strip has left the second vessel, it is rinsed with water in the rinsing chamber 28, drained by means of the rollers 30 and dried in the drying chamber 31.

From the above treatments, there is produced an aluminum strip of which roughened surface shows an average grain roughness of 0.64 microns and white colored appearance. This aluminum strip is cutted into sheets of an appropriate length, and the sheets are photosensitized by application of a liquid preparation comprising a light-sensitive diazo-resin which is known as available for the manufacture of the wipe-on type offset printing plates. After drying, the photosensitized sheets are imagewise exposed to actinic light from a carbon arc lamp for 3 minutes under a negative pattern combined with a gray scale with dot (200 lines per inch). The aluminum sheets are then developed, rinsed with water and coated with gum arabic to give a hydrophilic surface so that the offset printing plates are thus produced.

These offset printing plates show a good reproducibility of printed dots, as the printed dots are reproduced accurately in the copies even in any minute image parts thereof. When a printing process is made using these offset printing plates set up in an offset printing machine, 20,000 copies of perfectly uniform quality can be obtained from each plate without involving any reduction in the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 7

The process of Example 6 is repeated except that the

polyethyleneglycol octylphenyl ether (the non-ionic surface active agent) present in the aqueous electrolyte employed is replaced by polyethyleneglycol nonylphenyl ether; polyethyleneglycol dodecylphenyl ether; polyethyleneglycol oleylether; polyethyleneglycol laurylether; polyethyleneglycol di-stearate; polyethyleneglycol mono-stearate and polyethyleneglycol monolaurate, respectively. There are obtained such uniformly roughened aluminum strips which show an average grain roughness of 0.64 microns and a white colored appearance at the roughened surface thereof. From these roughened aluminum strips are produced offset printing plates in the same manner as described in Example 6. When a printing process is carried out using these plates in an offset printing machine, it is found that these offset printing plates can give 20,000 copies of perfectly uniform quality from each plate without changing the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 8

The process of Example 6 is repeated except that the electrolytes present in the first and second electrolysis vessels are replaced by such an aqueous electrolyte containing 2.5 percent by weight of hydrogen chloride, 0.1 percent by weight of polyethyleneglycol laurylether and 2.5 percent by weight of di-ethanol amine, respectively, and that both the first and second vessels are operated with an alternating electric current at a current density of 70 A/dm², at an electrolyte temperature of 25°C and at a residence time of 20 seconds for the aluminum strip in each vessel. There is obtained such uniformly roughened aluminum strip which shows an average grain roughness of 0.70 microns and a white colored appearance at the roughened surface. From this roughened aluminum strip are produced offset printing plates in the same manner as described in Example 6. When a printing process is carried out using these plates in an offset printing machine, it is found that these offset printing plates can give 20,000 copies of perfectly uniform quality from each plate without decreasing the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 9

The process of Example 8 is repeated using an aqueous electrolyte containing 2.5 percent by weight of hydrogen chloride, 0.1 percent by weight of polyethyleneglycol octylphenyl ether and 2.5 percent by weight of mono-ethanol amine in each of the first and second vessels. The results obtained are similar to those of Example 8.

EXAMPLE 10

The process of Example 8 is repeated using an aqueous electrolyte containing 2.5 percent by weight of hydrogen chloride, 0.1 percent by weight of polyethyleneglycol mono-stearate and 2.5 percent by weight of tri-ethanol amine in each of the first and second vessels. The results obtained are similar to those of Example 8.

EXAMPLE 11

The process of Example 6 is repeated except that an aqueous electrolyte containing 2 percent by weight of

hydrogen chloride, 0.08 percent by weight of polyethyleneglycol nonylphenyl ether, 3 percent by weight of tri-ethanol amine and 1.5 percent by weight of aluminum chloride is used in each of the first and second vessels, and that both the first and second vessels are operated with an alternating electric current at a current density of 60 A/dm² at an electrolyte temperature of 25°C and at a residence time of 17 seconds for the aluminum strip in each vessel. There is obtained such a uniformly roughened aluminum strip which shows an average grain roughness of 0.73 microns and a white appearance at the grained surface.

From this roughened aluminum strip are produced offset printing plates in the same manner as described in Example 6. When a printing process is carried out using these plates in an offset printing machine, it is found that these offset printing plates can give 20,000 copies of perfectly uniform quality from each plate without changing the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 12

The process of Example 6 is repeated except that an aqueous electrolyte containing 3 percent by weight of hydrogen chloride, 0.1 percent by weight of polyethyleneglycol octylphenyl ether and 5 percent by weight of aluminum chloride is used in each of the first and second vessels, and that both the first and second vessels are operated with an alternating electric current at a current density of 80 A/dm² at an electrolyte temperature of 20° - 25°C and at a residence time of 20 seconds for the aluminum strip in each vessel. There is obtained such a uniformly roughened aluminum strip which shows an average grain roughness of 0.60 microns and a white colored appearance at the grained surface. From this roughened aluminum strip are produced offset printing plates in the same manner as described in Example 6. When a printing process is carried out using these plates in an offset printing machine, these offset printing plates can give 20,000 copies of perfectly uniform quality from each plate without producing any variation in the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 13

The process of Example 12 is repeated except that an aqueous electrolyte containing 3 percent by weight of hydrogen chloride, 0.1 percent by weight of polyethyleneglycol octylphenyl ether, 2.5 percent by weight of mono-ethanol amine and 5 percent by weight of magnesium chloride is used in both the first and second vessels. The results obtained are similar to those of Example 12.

EXAMPLE 14

A continuous strip S of aluminum which is 300 mm wide and 0.3 mm thick is electrolytically treated in a series of the first electrolysis vessel 1 and second electrolysis vessel 2 of the plant as shown in FIG. 1 in the following manner.

The aluminum strip S is continuously fed into the first electrolysis vessel 1 containing an electrolyte which is an aqueous solution of 3 percent by weight of hydrogen chloride, 10 g/l. of tri-ethanol amine and 1 g/l. of poly-

thylene glycol octylphenyl ether (a non-ionic surface-active agent) in the cavity thereof. The temperature in the electrolyte is maintained at $30^{\circ} \pm 1^{\circ}\text{C}$. By effecting electrical connections between the terminals *g* and *i*, between the ones *h* and *l*, between the ones *a* and *c*, and between the ones *b* and *c*, alternating electric current is supplied to the electrodes 3 and 4 of graphite so that the electrolyte is flown through by an alternating current at a current density of 20 A/dm^2 . While submerged in the electrolyte bath, the aluminum strip *S* advances continuously to pass below the lower side of the electrode 3, through the orifice 8 in the intermediate wall 4 and then below the lower side of the electrode 4 at such a speed that the residence time of the aluminum strip within this first electrolysis vessel is 35 seconds. The electrolyte is supplemented at a total rate of 100 litres/min. from the opposite pairs of the nozzles 32 and 33.

The aluminum strip which has left the first electrolysis vessel 1 is then rinsed with water in the rinsing chamber 27 and passed between the draining roller to remove the water layer which is adhering on the roughened surface of the aluminum strip. The aluminum strip is subsequently fed into the second electrolysis vessel 2 containing an electrolyte essentially consisting of an aqueous solution of 15 percent by weight of sulfuric acid at a temperature of 30°C , and it is submerged and runs within the electrolyte bath to pass successively below the lower side of the electrode 3', through the orifice 8' in the intermediate wall and below the lower side of the electrode 4' of the second vessel 2. The arrangement and dimensions of these opposite electrodes 3' and 4' as well as the intermediate wall and its orifice in the second vessel 2 are the same as those of the corresponding members in the first vessel 1. By effecting electrical connections between the terminals *n* and *q*, between the ones *p* and *r*, between the ones *s* and *w* and between the ones *u* and *x*, alternating electric current is supplied to the electrodes 3' and 4' in the second vessel, so that the electrolyte is flown through by an alternating current at a current density of 4 A/dm^2 in the second vessel. The aluminum strip passes through the second vessel at such a speed that the residence time of the aluminum strip therein is 35 seconds. After the aluminum strip is anodized in the second vessel, it is rinsed with water in the rinsing chamber 28, drained by means of the rollers 30 and dried in the drying chamber 31.

From the above treatments, there is produced an aluminum strip in which an anodized oxide film of 0.20 microns thick has been formed over the uniformly roughened surface of the strip. The roughened aluminum surface appear white shows an average grain roughness of 0.50 microns. This aluminum strip is cut into sheets of an appropriate length, and the sheets are photosensitized, imagewise exposed to actinic light under a negative pattern and a gray scale with dot and developed in a conventional manner to produce offset printing plates.

When a printing process is made using these plates set up in an offset printing machine, it is found that these offset printing plates can give more than 20,000 copies of perfectly uniform quality from each plate without decreasing the reproducibility of the printed dots and without showing any contamination on the printing surface of the plate.

EXAMPLE 15

The process of Example 14 is repeated except that the electrical connections are created between the terminals *g* and *j*, between the ones *h* and *l*, between the ones *a* and *d* and between the ones *b* and *f* to pass an alternating electric current at a current density of 60 A/dm^2 through the electrolyte in the first electrolysis vessel, that the electrical connections are made between the terminals *n* and *q*, between the ones *p* and *r*, between the ones *t* and *w* and between the ones *v* and *x* to pass an alternating electric current at a current density of 60 A/dm^2 through the electrolyte in the second electrolysis vessel and that the temperature in the electrolyte bath is kept at 50°C in the second electrolysis vessel.

When the treatments are carried out under the above-mentioned conditions, there is produced an aluminum strip in which an anodized oxide film of 0.55 microns thick has been mounted over the uniformly roughened surface of the aluminum strip with an average grain roughness of 0.78 microns and a white appearance at the roughened aluminum surface. The roughened and anodized aluminum strip is then cut into sheets of an appropriate length, and the sheets are processed into offset printing plates in a common manner by photosensitizing, photographically exposing to actinic light under a negative pattern and gray scale with dot and developing in a conventional way. When a printing process is carried out using these offset printing plates set up in an offset printing machine, it is found that these plates show a very much excellent stability to print numerous copies of perfectly uniform quality.

EXAMPLE 16

The process of Example 14 is carried out in the same manner as in Example 14 but except that switching is made to make electric connections between the terminals *m* and *q*, between the ones *o* and *r*, between the ones *s* and *w* and between the ones *u* and *x* to pass a direct electric current at a current density of 2.0 A/dm^2 through the electrolyte in the second electrolysis vessel, and that an alternating electric current is passed at a current density of 60 A/dm^2 through the electrolyte in the first electrolysis vessel.

From the above treatments, there is produced a roughened and anodized aluminum strip in which an anodized oxide film of 0.18 microns thick is formed over the uniformly roughened surfaces of the strip with an average grain roughness of 0.76 microns and a white appearance at the roughened surface thereof. The aluminum strip thus treated is cut into sheets of an appropriate length and the resulting sheets are each processed into an offset printing plate by photosensitizing, photographically exposing to light and then developing in a conventional manner. When a printing process is carried out using the resultant offset printing plate set up in an offset printing machine, it shows a very much excellent service life to yield numerous copies of perfectly uniform quality.

EXAMPLE 17

The process of Example 14 is followed except that the electrolyte in the second vessel is replaced by an electrolyte of the same composition as that of the elec-

trollyte in the first vessel and that the conditions of operating the first and second vessels are changed as follows:

Electrical connections are made between the terminals *g* and *j* between the ones *h* and *l*, between the ones *a* and *d* and between the ones *b* and *f* to pass an alternating electric current at a current density of 80 A/dm² through the electrolyte bath in the first vessel. The speed of advance of the aluminum strip is increased so that the residence time of the strip is 17 seconds in the first and second electrolysis vessels, respectively.

Electrical connections are created between the terminals *n* and *q*, between the ones *p* and *r*, between the ones *t* and *w* and between the ones *v* and *x* to pass an alternating electronic current at a current density of 80 A/dm² through the electrolyte bath in the second vessel. The speed of advance of the aluminum strip is increased so that the residence time of the strip is 17 seconds in the first and second vessels, respectively.

From the above treatments, there is produced a roughened and anodized aluminum strip of which surfaces have been uniformly roughened to an average grain roughness of 0.66 microns and show a white appearance. This roughened and anodized aluminum strip is cut into sheets of an appropriate length, and these sheets are processed into offset printing plates in a conventional manner by photosensitizing, photographically exposing to actinic light and then developing in a conventional way. When a printing process is carried out using these plates in an offset printing machine, it is found that these offset printing plates exhibit a very much high stability to print numerous copies of perfectly uniform quality.

EXAMPLE 18

This example illustrates a continuous production of an offset printing plate according to the process of the present invention by means of the plant which is shown in FIG. 2 of the accompanying drawing.

A continuous strip *S* of aluminum which is 300 mm wide and 0.3 mm thick is electrolytically treated in a series of the first electrolysis vessel 1 and second electrolysis vessel 2 in the following manner. following manner.

The aluminum strip *S* is continuously fed into the first electrolysis vessel 1 containing an aqueous electrolyte containing 3 percent by weight of hydrogen chloride, 10 g/l. of tri-ethanol amine and 1 g/l. of polyethyleneglycol octylphenyl ether (a non-ionic surface-active agent) in the cavity thereof. The temperature in the electrolyte is maintained at 30° ± 1°C. By effecting electrical connections between the terminals *g* and *i*, between the ones *h* and *l*, between the ones *a* and *c*, and between the ones *b* and *c*, alternating electric current is supplied to the electrodes 3 and 4 of graphite so that the electrolyte is flown through by an alternating current as a current density of 20 A/dm². While submerged in the electrolyte bath, the aluminum strip *S* advances continuously to pass through the slot 5 in the electrode 3, through the orifice 8 in the intermediate wall 4 and then through the slot 6 in the electrode 4 at such a speed that the residence time of the aluminum strip within this first electrolysis vessel is 35 seconds. The slots 5, 6 and the orifice 8 are aligned with each other at the same level over the bottom of the vessel and each have such dimensions that the advancing aluminum strip can freely pass therethrough without contacting

with the materials of the electrodes and the intermediate wall. The dimensions of the orifice 8 are such that the depth of orifice is 20 mm and that the distance between the upper boundary of the orifice and the upper side of the aluminum strip, the distance between the lower boundary of the orifice and the lower side of the aluminum strip and the distances between the two lateral sides of the aluminum strip and the lateral boundaries of the orifice are 25 mm, respectively. The horizontal, cross-sectional areas of the electrodes 3 and 4 in the plant of FIG. 2 are equal to those of the electrodes 3 and 4 in the plant of FIG. 1. The electrolyte is supplemented at a total rate of 100 litres/min. from the opposite pairs of the nozzles 32 and 33.

The aluminum strip which has left the first electrolysis vessel 1 is then rinsed with water in the rinsing chamber 27 and passed between the draining roller to remove the water layer which is adhering on the roughened surface of the aluminum strip. The aluminum strip is subsequently fed into the second electrolysis vessel 2 containing an electrolyte essentially consisting of an aqueous solution of 15 percent by weight of sulfuric acid at a temperature of 30°C, and it runs within the electrolyte bath to pass successively through the slot 5' in the electrode 3', through the orifice 8' in the intermediate wall and through the slot 6' in the electrode 4' of the second vessel 2. The arrangement and dimensions of these opposite electrodes and their slots as well as the intermediate wall and its orifice in the second vessel 2 are the same as those of the corresponding members in the first vessel 1. By effecting electrical connections between the terminals *n* and *q*, between the ones *p* and *r*, between the ones *s* and *w* and between the ones *u* and *x*, alternating electric current is supplied to the electrodes 3' and 4' in the second vessel, so that the electrolyte is flown through by an alternating current at a current density of 4 A/dm² in the second vessel. The aluminum strip passes through the second vessel at such a speed that the residence time of the aluminum strip therein is 35 seconds. After the aluminum strip is anodized in the second vessel, it is rinsed with water in the rinsing chamber 28, drained by means of the rollers 30 and dried in the drying chamber 31.

From the above treatments, there is produced an aluminum strip in which an anodized oxide film of 0.20 microns thick has been formed over each of the uniformly roughened surfaces of the strip. The roughened aluminum surfaces appear white and show an average grain roughness of 0.50 microns. This aluminum strip is cutted into sheets of an appropriate length, and the sheets are photosensitized, imagewise exposed to actinic light under a negative pattern and a gray scale with dot and developed in a conventional manner to produce offset printing plates.

When a printing process is made using these plates, it is found that these printing plates have a very much good service-life or stability in practice.

What we claim is:

1. A process of producing an aluminum base offset printing plate, which comprises a step of roughening the surface of an aluminum base sheet by electrolytically treating it with an alternating electric current at a current density of 10 - 80 A/dm² in an electrolyte consisting of an aqueous solution containing 1 - 3 percent by weight of hydrochloric acid (calculated as

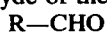
HCl) and a total concentration of 0.05 percent – 5 percent (by weight based on the entire weight of said aqueous solution) of at least one anti-corrosive agent selected from a mono-amine of the formula:



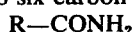
wherein (i) R_1 , R_2 and R_3 are each an alkyl group of one to six carbon atoms, or (ii) R_1 and R_2 are each an alkyl group of one to six carbon atoms but R_3 is a hydrogen atom, or (iii) R_1 is an alkyl group of one to six carbon atoms, a carboxyl group or hydroxyl group but R_2 and R_3 are each a hydrogen atom, or (iv) R_1 , R_2 and R_3 are each a hydroxyethyl group $-C_2H_4OH$, or (v) R_1 and R_2 are each a group $-C_2H_4OH$ and R_3 is a hydrogen atom, or (vi) R_1 is a group $-C_2H_4OH$ but R_2 and R_3 are each a hydrogen atom; a di-amine of the formula:



wherein R is an alkylene group of the formula $-C_nH_{2n}-$ and n is a whole number of 1 to 6; an aliphatic aldehyde of the formula:



wherein R is a hydrogen atom or an alkyl group of one to six carbon atoms; an amide of the formula:



wherein R is a hydrogen atom or an alkyl group of one to three carbon atoms; urea, chromic acid and the known non-ionic surface active agents.

2. A process as claimed in claim 1 in which the electrolyte employed contains at least one mono-amine of the formula



as defined in the claim 1 for the anti-corrosive agent.

3. A process as claimed in claim 1 in which the electrolyte employed contains at least one di-amine of the formula



as defined in the claim 1 for the anti-corrosive agent.

4. A process as claimed in claim 1 in which the electrolyte employed contains at least one aliphatic aldehyde of the formula



as defined in the claim 1 for the anti-corrosive agent.

5. A process as claimed in claim 1 in which the electrolyte employed contains at least one amide of the formula



as defined in the claim 1 for the anti-corrosive agent.

6. A process as claimed in claim 1 in which the electrolyte employed contains urea as the anti-corrosive agent.

7. A process as claimed in claim 1 in which the electrolyte employed contains chromic acid as the anti-corrosive agent.

8. A process as claimed in claim 1 in which the electrolyte employed contains at least one known non-ionic surface-active agent as the anti-corrosive agent at a concentration of 0.05 percent to 1 percent by weight based on the entire weight of the electrolyte.

9. A process as claimed in claim 1 in which the elec-

trolyte employed contains also at least one selected from magnesium chloride, aluminum chloride, zinc chloride and ammonium chloride as a secondary etching agent at a total concentration of the chloride ions of up to 8 percent by weight of the entire weight of the electrolyte.

10. A process as claimed in claim 1 in which the electrolytic treatment of the aluminum base sheet with an alternating electric current in the electrolyte containing hydrochloric acid as the primary etching agent and at least one anti-corrosive agent is effected for a time of 20 to 60 seconds at a temperature of $20^\circ - 30^\circ C$.

11. A process as claimed in claim 1 in which an alternating electric current having a current density of 40 – 70 A/dm² is used for the electrolytic treatment of the aluminum base sheet.

12. A process as claimed in claim 1 in which the process further comprises a subsequent step of anodizing the roughened surface of the aluminum sheet which is carried out in a known manner.

13. A process as claimed in claim 1 in which the process further comprises a subsequent step of anodizing the roughened surface of the aluminum sheet which is carried out in a known manner, followed by a more further step of causing finely divided silica particles to be deposited and adsorbed by the anodized, roughened surface of the aluminum sheet.

14. A process for the continuous production of an aluminum base offset printing plate, which comprises a step of roughening the surface of an aluminum base sheet in the form of a continuous strip in a continuous manner by electrolytically treating the aluminum strip with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an electrolyte essentially consisting of an aqueous solution containing 2 – 3 percent by weight of hydrogen chloride, 0.05 – 0.5 percent by weight of a non-ionic surface-active agent which may preferably be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, up to 5 percent by weight of a mono-amine of the formula



as defined in the claim 1 which may preferably be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, and up to 5 percent by weight of aluminum chloride or magnesium chloride, while advancing the aluminum strip continuously through the bath of said electrolyte in an elongated electrolysis vessel containing the electrolyte bath in the cavity thereof, wherein the cavity of the electrolysis vessel is substantially divided into two sections by an intermediate vertical wall which locates substantially at the middle of the longitudinal axis of the vessel, which extends across the whole width of the vessel and which contains a communicating orifice adapted to insure that the aluminum strip is freely passed through said orifice with keeping the aluminum strip submerged in the electrolyte bath and that the electrolyte is allowed to freely flow through said orifice to make a communication between the above-mentioned two sections of the vessel cavity, and wherein each of these two sections of the vessel cavity contains therein at least one electrode of which

one surface is faced to and spaced from the surface of the advancing aluminum strip to be roughened.

15. A process as claimed in claim 14 in which the aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride and 0.05 – 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such arrangement as defined in the claim 14.

16. A process as claimed in claim 14 in which the aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, 0.05 – 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, and up to 5 percent by weight of aluminum chloride or magnesium chloride, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongate electrolysis vessel of such arrangement as defined in the claim 14.

17. A process as claimed in claim 14 in which the aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, 0.05 – 0.5 percent by weight of a non-ionic surface-active agent

which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, and 0.05 – 0.5 percent by weight of a monoamine which may be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such an arrangement as defined in the claim 14.

18. A process as claimed in claim 14 in which the aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 80 A/dm² for a time of 15 – 60 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, 0.05 – 0.5 percent by weight of a non-ionic surface-active agent which may be selected from polyethyleneglycol alkylphenyl ethers, polyethyleneglycol alkylethers and fatty acid esters of polyethyleneglycol, 0.05 – 5 percent by weight of a mono-amine which may be selected from mono-ethanol amine, di-ethanol amine and tri-ethanol amine, and up to 5 percent by weight of aluminum chloride or magnesium chloride, while advancing the aluminum strip continuously in the submerged condition through the bath of said electrolyte in an elongated electrolysis vessel of such an arrangement as defined in the claim 14.

19. A process as claimed in claim 14 in which the aluminum strip is roughened in a continuous manner by electrolytically treating with an alternating electric current at a current density of 40 – 70 A/dm² for a time of 20 – 30 seconds in an aqueous electrolyte containing 2 – 3 percent by weight of hydrogen chloride, up to 3 percent by weight of aluminum chloride, 0.5 – 3 percent by weight of tri-ethanol amine and 0.05 – 0.1 percent by weight of a non-ionic surface-active agent which may preferably be polyethyleneglycol octylphenyl ether.

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