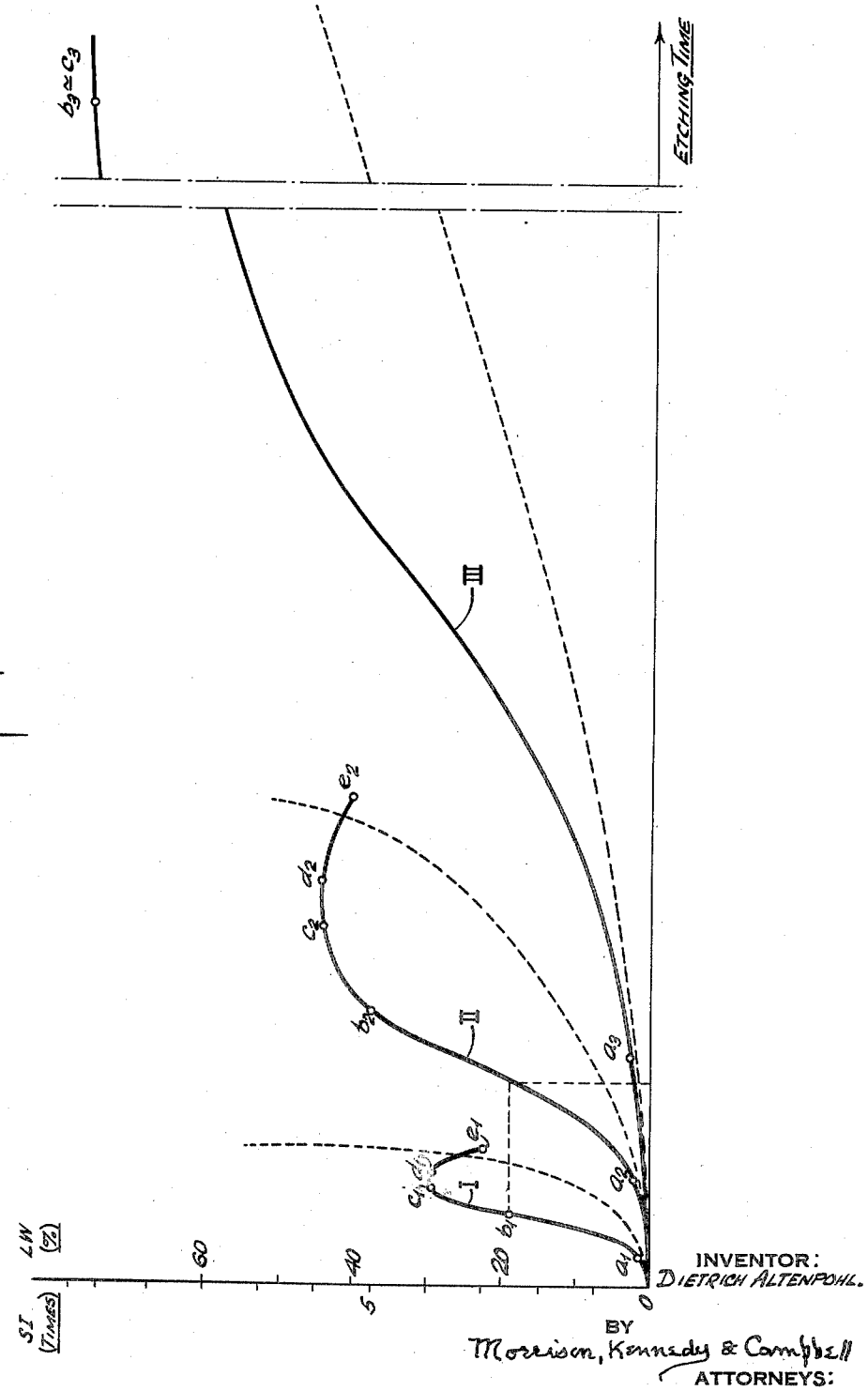
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METHOD OF ETCHING ALUMINUM FOILS

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Fig. 1.



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METHOD OF ETCHING ALUMINUM FOILS

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Fig. 2.

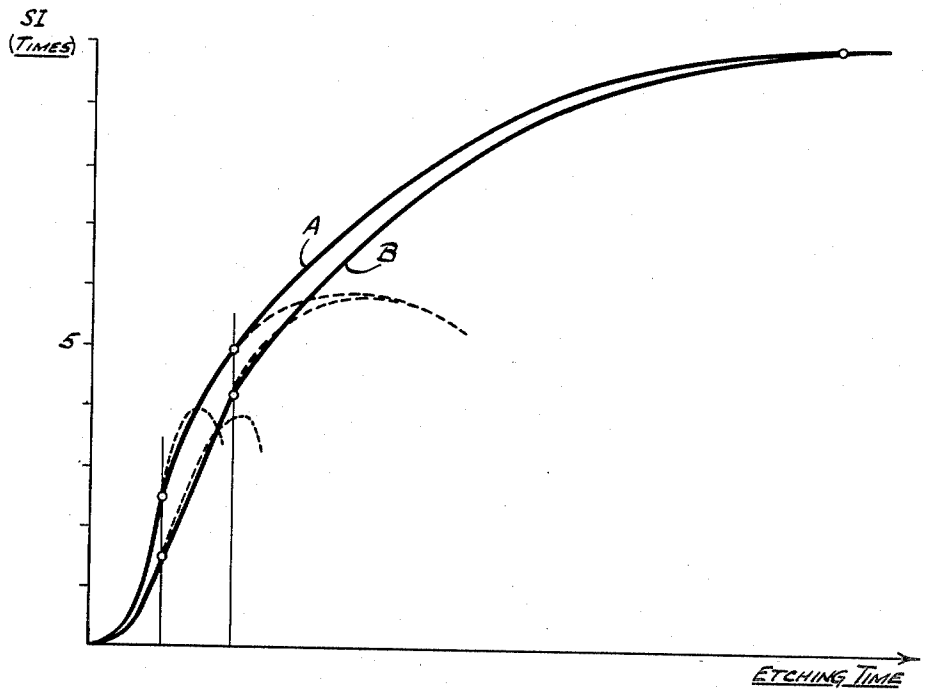
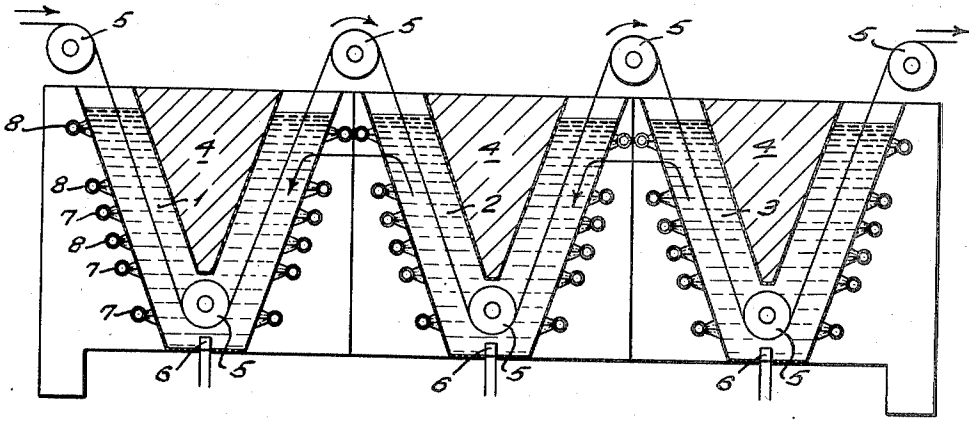


Fig. 3.



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METHOD OF ETCHING ALUMINUM FOILS

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2 Claims. (Cl. 41—42)

The present invention relates to etching methods for increasing the surface area of aluminum foil which is to be used in electrolytic condensers.

The treatment of aluminum foil by chemical etching to multiply the effective surface area thereof has been practiced commercially for many years. In such methods, the foil is generally pickled in an alkaline solution to remove rolling oils, oxide skins and other disturbing surface impurities, then immersed in the etching bath containing hydrochloric acid and thereafter submitted to a cleaning process and dried.

There are at least two well known methods of carrying out the etching treatment, namely, batch etching and continuous etching. According to the batch etching method, the foil strip is either coiled or cut into sheets of limited size and fixed on jigs or clamps, immersed by means of these jigs or clamps successively into a pickling bath, an etching bath and one or more cleaning baths and then dried. According to the continuous etching method, the aluminum foil is fed as a strip successively through the pickling, etching and cleaning baths and thereafter through a drying device. With the latter method, the etching time needed for the desired roughening is controlled, ordinarily, by the speed of travel of the foil through the etching bath, inasmuch as the length of the bath itself cannot be easily varied.

In producing aluminum foil for electrolytic condensers, one should strive for a roughened foil of about 0.1 mm. thickness made from an aluminum of a high purity, for example, in the range of 99.80 and 99.99%, the active surface of the foil having been increased by eight to twelve times by etching. Uniformity of the roughened aluminum foil should be maintained with variances less than ±5%. In practice, a method is desirable which makes it possible to obtain consistently such a roughened aluminum foil with a minimum of supervision and above all in an etching time as short as possible.

In accordance with present etching methods, to obtain a high degree of uniformity of the roughened aluminum foil, etches of relatively low aggressiveness are employed with the result that the etching time is greatly prolonged; however, if etching solutions of greater aggressiveness were to be employed, the uniformity of the final product would be subject to great fluctuations and, in addition, the amount of supervision required would be greatly increased.

The present invention provides a method of etching aluminum foil to increase the effective surface thereof, whereby the time required for the etching process is reduced from approximately 20 to 150 minutes to approximately 4 to 10 minutes, and this without sacrificing the uniformity of the product and without necessary increase in the extent of supervision.

For a complete understanding of the present invention, reference may be had to the detailed description which follows, and to the accompanying drawings wherein:

Fig. 1 is a graphical representation showing the variation of surface area (SI) and the loss of weight (LW) with the time during which the foil is subjected to the etch; the curves in solid lines depict the surface variation, and the curves in dotted lines, the loss of weight for the duration of the etching time;

Fig. 2 is a graphical representation of the variation of surface area with etching time of two aluminum foils A and B having the same purity but different etching

properties wherein, in accordance with the present invention, the etching has been done in three successive stages, using at each stage an etch of reduced activity or aggressiveness; the dotted lines represent the characteristics of the more aggressive etching solutions of the first two stages if the etching were continued with the same etching solution instead of a less aggressive etching solution; and

Fig. 3 is a schematic cross-sectional representation of apparatus which may be employed in practicing the present invention.

It is well known that the aggressiveness or speed of action of an etch may be increased in a number of ways, such as by increasing the temperature and/or /concentration of the etch, or by subjecting the etch to an electrical current. Either direct or alternating current may be employed, and it may even be advantageous to employ both direct and alternating current simultaneously.

In Fig. 1, the curves I, II and III correspond to the values obtained at decreasing temperatures. These curves show that the reaction of the acid on the aluminum after immersion of the foil is slow at first. Thus, the etching progresses slowly during the "period of incipience," that is, up to the points a_1, a_2 and a_3, after which the surface area and the weight loss increase at a rapid rate, until the surface begins to break down or deteriorate. Further etching will result in a decrease of surface area, although the rate of loss of weight continues to increase. By a comparison of the points c_1, c_2 and c_3, representing the maximum surface area, it will be observed that greater surface areas are possible with slower acting etches. The higher the activity of the acid, the sooner an overetching (beginning at d_1 and d_2) will occur; this, of course, is undesirable for obtaining a good roughening. Such an overetching causes, on the one hand, a decrease of the roughness by removing projecting spots of the surface, and on the other side, a rapid increase of the loss of weight. Soon after the beginning of the overetching, often within a few seconds, a complete corrosion of the foil takes place (point e_1 or e_2). As a matter of fact, as soon as the heat of reaction cannot be eliminated quickly enough by the reacting surface, the etching process quickly accelerates as a result of local temperature increase.

Very aggressive acids not only increase the danger of overetching, but as already mentioned, cause a non-uniform, unequal roughening. Within one aluminum foil strip, or among several strips there are always certain differences in the physico-chemical properties, and these differences often cause the strips to react differently to a given etching treatment. When etches of higher aggressiveness are used, the degree of control is less. If one tries to carry out the etching under conditions which make it possible to reach the maximum surface increase, there is the danger that certain spots of the foils will become overetched and corrode. In view of the danger of overetching, it is possible to use in practice the etching time only up until the point b_1, b_2 or b_3. Moreover, when a strong acid is used, the fluctuations of the final roughening surface are objectionably high, say, ±15%.

On the other hand, one can see from a comparison of the curves I and III of Fig. 1 that the conditions become more and more stable when the etching process is carried out with a slow or less aggressive etch; experiments have shown that the etching can be uniformly reproduced with different foils with variations of effective surface area about ±5%, while at the same time obtaining greater absolute value of surface area and without risk of overetching. Actually, in practice, overetching with less aggressive etches does not occur, so that the etching time b_3 makes it possible to obtain nearly the maximum roughness; however, the etching time is so greatly prolonged that it is impractical for commercial use, especially for continuous etching methods. Up to now, continuous chemical etching methods with moderately aggressive etches have been employed (see curve II of Fig. 1) as a compromise, however, variations of ±10% in the final surface area are obtained, even with high purity aluminum and these are generally considered unsatisfactory by the manufacturers of high-grade electrolytic condensers.

Ideally, the roughening speed should, after a period of

incipience as short as possible, reach high values and then turn to a stable course, that is to say, it should approach an asymptotic value. In practice, however, when foils pass through a single etching bath, the reaction of the acid on the aluminum does not take place in any appreciable measure until after the end of the period of incipience, which may be over one-fourth of the total etching time, and thereafter takes place actively approaching the over-etch stage when the foil leaves the etching bath. Consequently, for the industrial manufacture of etched foil, by a single stage method, only the middle part of the etching time spent is valuable.

According to my present invention the aluminum foils are roughened in two or more baths ("stage etching"), the aggressiveness of the etching solution being reduced substantially from bath to bath. In the first bath I reduce the period of incipience and increase the active surface as quickly as possible by means of a very aggressive acid and, thereafter, I slowly deepen the roughness, for instance, by means of a weaker or colder acid, without destroying the projecting spots already formed on the surface. In this way I achieve the apparently impossible combination of a short etching time and a high and uniformly reproducible roughening, as shown in Fig. 2, in which curves representing the surface increase of two aluminum foils A and B having the same purity but different etching properties are plotted in relation to time of etching, the etching being done in three stages using a less aggressive etch in each stage. The curves are not superimposed because different aluminum foils, although of the same purity, always show differences in etching properties.

Fig. 2 illustrates the main advantages of such a multi-stage etching wherein the aggressiveness of the acid is reduced from stage to stage. The etching time is utilized as economically as possible, the objective being a high initial etching speed after a short period of incipience and a very great increase in effective surface area which can be consistently reproduced with uniformity of results and product. Differences in the roughening speed of certain elementary areas are largely equalized; this equalization is caused by the stable final phase of the etching.

In carrying out the multi-stage etching according to my invention, direct or alternating current may be employed in order to promote the etching of the earlier stages, either for the duration of one or more etching stages and/or a part of one or more etching stages. In addition, substances, such as sulphates, sulphuric acid, nitric acid, and salts of metals which are nobler than aluminum, may be added to retard or promote the reaction.

The following examples illustrate the invention.

Example 1

A foil made from electrolytically refined aluminum with a purity of 99.99% was used. After pickling in caustic soda solution the foil became roughened in a first stage during 110 seconds in a 30° C. warm bath obtained by mixing 400 cc. of 32% HCl, 100 cc. concentrated HNO_3, and 100 grams $FeCl_3$ with a litre of water containing 15 grams Al per litre. (Here and in other places of the examples relating to the aluminum content of the etching solution the symbol Al does not mean metallic aluminum, but aluminum cations.) After the first etching, the surface increase (measured according to the German standard DIN 41330, 4th edition) was five and one-half times the original area. Thereafter the etching was continued during 120 seconds in a 25° C. warm bath consisting of a solution of 10% hydrochloric acid containing about 10 grams Al per litre. In this second stage the surface area was increased to eight times its original area.

Example 2

A foil of high-purity aluminum (99.97% Al, remainder Fe and Si) which had been pickled in caustic soda solution, was etched thereafter in a first stage during 90 seconds in 33° C. warm, 15% hydrochloric acid containing 50 g. $FeCl_3$ and 10 g. Al per litre, a three fold roughening being obtained. In the second stage, the roughening was continued during 4 minutes in 20° warm, 20% hydrochloric acid with 50 g. Al per litre, the surface area was increased to seven times its original area.

Example 3

A foil of high-purity aluminum (99.97% Al, remainder Fe and Si), which has been pickled in caustic soda solution was etched thereafter in a first stage at a temperature of 65° C. in a 12% hydrochloric acid containing 12 g. Al per litre and 10 g. $FeCl_3$ per litre, a six fold roughening being obtained. Thereafter the etching was terminated in a second stage at 40° C. in 12% hydrochloric acid solution containing 10 g. Al per litre. In this second stage a ten fold total surface increase (with fluctuations of uniformity of ±4%) was obtained. The etching time was 150 seconds in the first stage and 250 seconds in the second stage. In a single stage only it was not possible with this high-purity foil, even in a multiple of the mentioned etching time, to obtain even approximately the same high and uniform roughening, although many different acid mixtures were used.

The present invention can be carried out by both the batch and continuous etching methods. The continuous etching method, however, can be made largely automatic, and in Fig. 3 a three-stage etching device suitable for this purpose is shown schematically in longitudinal section. For carrying out the stage etching, the pickled aluminum foil strip is pulled through the three acid troughs **1**, **2** and **3** made from sheet steel coated with rubber and provided with the wedge-shaped displacing bodies **4** from the same material. After leaving the stage etching device, the foil strip is washed and dried. The guide rollers **5** are made, for instance, from glass or china. The reference numeral **6** designates contact thermometers which control automatically the heating and the cooling of the single troughs by means of relays. In the present example, the heating is effected by blowing steam through the nozzle rows **7** against the outside of the acid troughs. As soon as the steam duct is closed, the heating ceases immediately. The cooling is done by spraying water against the outside of the troughs through the nozzle rows **8**. Also in this case, the effect can be interpreted at once. Preferably the acid is moved relatively to the movement of the foil in the opposite direction in counterflow fashion.

On its way through the troughs the acid becomes slowly warmer, partly because of the chemical reaction, partly by the external heating, and becomes more and more enriched with aluminum. The action of the etch during its way through the single etchings stage may be controlled by the addition of a more concentrated etch or by substances such as iron salts. It is advantageous to employ narrow etching baths so that the temperature of the etching acid can be better regulated and its aluminum content kept low.

The angularly disposed V-shaped grouping of the acid baths according to Fig. 3 may, of course, be replaced wholly or partly by another grouping, for instance, by rectangular troughs, simplifying the construction of the device, but partly sacrificing the advantage of a high speed of the acid relative to the foil strip.

The essential feature of the present invention is a sequence of at least two roughening etchings, the aggressiveness of the acid solutions being reduced substantially from stage to stage. The usual baths which serve to clean the foil before or after the roughening process and effect only a negligible roughening do not belong to the roughening baths in the sense of the invention.

The etching in a largely automatic multi-stage etching device makes it possible to achieve a high, uniform and reproducible roughening in short etching times and with a minimum of supervision. The advantages over the customary single stage etching can be well appreciated when it is taken into consideration that the etching time required for obtaining a satisfactory roughening of high purity aluminum with a surface increase of eight to twelve fold by conventional single stage methods at bath temperatures of 0° C. to 35° C. is 20 to 150 minutes in comparison to 4–10 minutes with the present invention.

What I claim is:

1. In a method for etching aluminum foil for the purpose of increasing the surface area thereof, the steps of subjecting the surface of the foil to a plurality of successive surface increasing treatments with agents consisting essentially of non-oxidizing, aluminum dissolving, etching solutions, while reducing the aggressiveness of the etch from treatment to treatment, the surface increasing effects of the etching solutions on the aluminum surfaces having generally the characteristics involving a period of time consuming incipience during which the action of the etch is slow and a period of rapid surface increasing action following the period of incipience and before a maximum value of surface area is reached, the periods of incipience being of shorter duration for etching solutions

of high aggressiveness, and the maximum values of surface area being greater for etching solutions of low aggressiveness, the surface of the foil being treated with an etching solution of high aggressiveness during at least a substantial portion of the period of incipience to shorten the total etching time by more quickly initiating the period of rapid etching action, thereafter continuing the surface increasing action by treating the surface with at least one additional surface increasing etching solution of reduced aggressiveness during the period of rapid etching and before a maximum value of surface increase is achieved with the preceding etching treatment to obtain a more uniformly etched surface and a higher value of surface increase than would be possible with the preceding etching treatment, and terminating the last etching treatment prior to deterioration of the surface due to overetching.

2. In a method for etching aluminum foil for the purpose of increasing the surface area thereof, the steps of subjecting the surface of the foil to a plurality of successive surface increasing treatments with agents consisting essentially of non-oxidizing, aluminum dissolving, etching solutions, the surface increasing effects of the etching solutions on the aluminum surfaces having generally the characteristics involving a period of time consuming incipience during which the action of the etch is slow

and a period of rapid surface increasing action following the period of incipience and before a maximum value of surface area is reached, the periods of incipience being of shorter duration for etching solutions of high aggressiveness, and the maximum values of surface area being greater for etching solutions of low aggressiveness, the surface of the foil being treated with an etching solution of high aggressiveness during at least a substantial portion of the period of incipience to shorten the total etching time by more quickly initiating the period of rapid etching action, and thereafter continuing the surface increasing action by treating the surface of the foil with a plurality of etching solutions of progressively reduced aggressiveness, each etch being employed during the period of rapid etching action and before a maximum value of surface increase is achieved with the preceding etching treatment to obtain a more uniformly etched surface and a higher value of surface increase than would be possible with the preceding etching treatment, and terminating the last etching treatment prior to deterioration of the surface due to overetching.

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