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ELECTROLYTIC DEVICE

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Fig. 1.

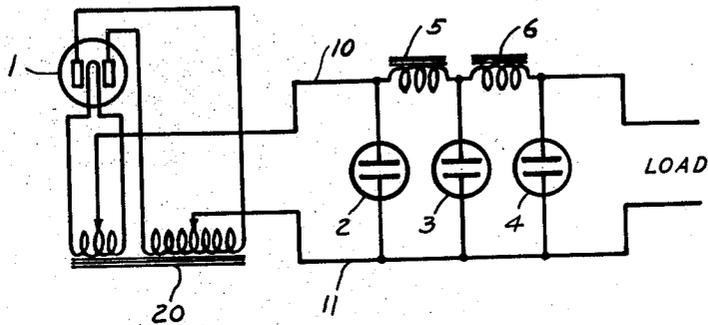
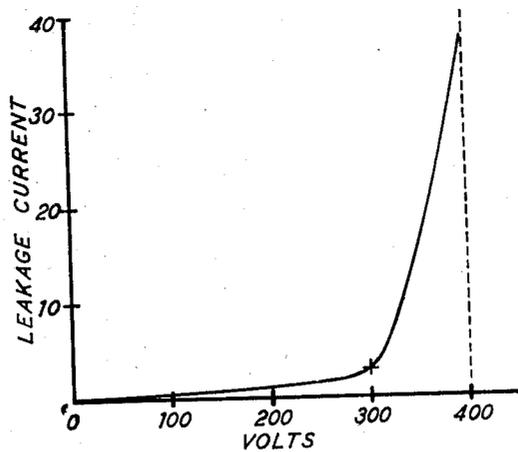


Fig. 2.



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## ELECTROLYTIC DEVICE

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9 Claims. (Cl. 175-315)

The present invention relates to electrolytic devices and more particularly to electrolytic condensers having novel and quite unique characteristics.

This application is a continuation in part of applicants' copending application Ser. No. 743,469, filed September 10, 1934, now Patent No. 2,122,393 and reissued as Re. 21,088.

It is a known phenomenon that when the voltage applied to an electrolytic condenser exceeds a certain limit, which as a rule corresponds approximately to the maximum voltage to which the condenser is formed, a spark discharge occurs at the film of the filmed electrode (or filmed electrodes) of the condenser, and at the same time the leakage current, which up to this "spark-ing voltage" is of a low value, sharply increases.

This sparking voltage of the condenser has been regarded as the limiting voltage, above which the condenser could not be operated. Not only is the sparking accompanied by an objectionable noise, but the sparking may greatly damage the film, both due to the mechanico-electrical effect characterizing sparking and because of the great heat development taking place directly in the vicinity of the film. This mechanism of sparking, as is well known, is the successive building up of a high voltage and the subsequent discharge across a spark-gap, which in the present instance is formed between the electrolyte and the film or the metallic surface disposed beneath the film. The mechanism of sparking and the relationship it bears to the present invention will be more fully described later.

For the above reasons it has been the practice to operate electrolytic condensers below the sparking voltage.

While to some extent, because of their well-known self-healing properties, electrolytic condensers can withstand, without detrimental effects transient voltages, which exceed their sparking voltage, such is only the case as long as the occurrence of such over-voltages is infrequent and of very short duration. In such cases no substantial cumulative heat development takes place and no substantial damage to the film is caused, and the small deteriorations of the film so caused, can be repaired by the self-healing action of the condenser.

However, in any application in which an electrolytic condenser is called upon to stand a voltage exceeding its normal operating voltage for periods of a few minutes or even a few seconds (or rapidly succeeding over-voltages of even

shorter duration), the condenser has to be designed for this higher voltage.

For instance, as will be more fully discussed later on, in radio sets, certain electrolytic condensers operate normally at about 250 to 300 volts; however, for a period of a few seconds after the set has been turned on, these condensers have to withstand voltages of 450 to 500 volts.

In the past such condensers had to be designed for these higher, short-duration voltages, which meant that they had to be formed at the higher voltages.

However, the formation of a 500-volt condenser is considerably costlier than that of a 300 volt condenser. Furthermore, as is well known, the capacity per unit of surface area decreases roughly, in proportion to the increase in forming voltage, and thus for a given capacity the electrode surface required is about  $\frac{500}{300}$  or about 1.66 times as great when formed at 500 volts, as when formed at 300 volts. The over-all dimensions of the condenser, and to a great extent its cost, increase in a similar manner for the higher voltage condensers.

The condensers according to our invention have the unique characteristic of altogether lacking a readily observable sparking voltage. Similarly to standard condensers, they do exhibit a sharp increase of the leakage current when the operating voltage exceeds a given "critical voltage", but this increase of current is not accompanied by sparking, nor by a substantial local heating up of the film surface. Or in other words, there is no breaking-down of the film at a large number of individual points as is characteristic of spark discharges, but merely the blocking action or insulating resistance of the film drops down uniformly to a value considerably lower than that which it possesses below this critical voltage.

Consequently, the film can stand, without being damaged, a voltage exceeding its critical voltage for any reasonable length of time, and even if a higher voltage is applied for several hours to the condenser and the condenser be ultimately damaged, this is because of the high current passing the condenser unduly heating up the condenser as a whole. If the condenser is to normally stand such over-voltage for quite extended periods, this can be taken care of by a more ample design of the condenser as a whole, whereby, however, only a comparatively small part of the above advantages obtained by the lower forming voltage, needs to be sacrificed.

The condenser of our invention, has a capacity corresponding to that of a condenser formed at

or near the critical voltage referred to above, although it need not necessarily have actually been formed at this voltage. For example, the film may be formed initially to a higher voltage than the critical voltage, and then be attacked, for example, by treatment in an alkaline solution as described in our Patent No. 2,035,022. Such a condenser when operated at or near the critical voltage will then assume the same capacity as if it had been formed at the critical voltage initially.

Thus while the "critical voltage" in both the condensers of the prior art and those made in accordance with our invention represents a voltage value above which the leakage current of the condenser sharply increases and at which its voltage current curve thus shows a pronounced bend or knee, in condensers of the prior art at or above such a "critical voltage" sparking takes place, whereas in our condensers no sparking takes place at the "critical voltage", and furthermore, as a rule, the leakage current increase at this voltage is much sharper than it is in prior art condensers.

Another distinction between our condensers and those of the prior art is as follows: When an electrode is operated in an electrolyte capable of forming it to a higher voltage (as in prior art condensers) and a voltage in excess of the original forming voltage is applied to the condenser, the electrode immediately begins to form to the higher voltage, and the initially large leakage current decreases as does the capacity of the condenser. In the case of our novel condenser, the leakage current remains substantially unchanged at its initial large value, or may even increase with time, without the condenser forming to the higher voltage or reducing its capacity.

Thus a condenser in accordance with our invention besides the absence of sparking, is also characterized by showing above the bend in its voltage-current characteristic curve, a high stable leakage current and a stable capacity.

We believe that the unique characteristics of the condensers of our invention may be explained as being brought about substantially in the following manner:

As is well known, the effective dielectric in electrolytic condensers consists of a thin dense film formed on the surface of the electrode, which dielectric film has a thickness corresponding to the critical voltage to which it is formed and to obtain the best results should be of high density and consist of substantially pure unhydrated oxide.

Such dielectric film contains minute pores or intercrystalline passages which, when the condenser is subjected to a voltage in excess of its critical voltage become filled with gas and behave to form minute spark gaps between the electrolyte and the electrode. When these gaps are broken down they form the centers of localized heat which tends to destroy the dielectric properties of the oxide film in their immediate vicinity. Moreover, when such gaps break down they produce the characteristic noise which in the art has come to be known as "scintillation."

In the condenser of our invention the formation of these minute spark gaps is prevented and no localized breakdown of the dielectric film can take place. One method of preventing the formation of such spark gaps which we have found is to provide on the dielectric film a thin layer of hydrated aluminum oxide or aluminum hydroxide which effectively blocks the surface of the film

and fills any minute pores contained therein. Thus with such a "blocked" dielectric film no gas can accumulate therein and localized breakdown cannot occur.

This hydrated layer may be formed electrolytically in a suitable electrolyte or may be formed by chemical transformation, i. e. hydration of the outer surfaces of the dense unhydrated oxide layer previously formed on the aluminum surface.

Since the density of the unhydrated aluminum oxide film is of the order of magnitude of 3.5, and the density of aluminum hydroxide is approximately 2.4, whereas the molecular volumes of these substances are in the ratio of approximately 1 to 2 respectively, it is evident that the conversion of the aluminum oxide to aluminum hydroxide produces an increase in volume of such magnitude that the conversion of only a small amount of unhydrated aluminum oxide is required to substantially completely fill up the pores contained in the film. Because the amount of unhydrated oxide which is converted is so small, the effective thickness of the dielectric layer is not materially affected.

A condenser in accordance with our invention may also be obtained by operating a filmed electrode provided with a dense unhydrated oxide dielectric film, in an electrolyte which is incapable of forming good dielectric film.

The characteristics of this operating electrolyte are such that it imparts to the film or to any gas bubbles which may form in the pores of the film, a negative zeta potential having a low value as compared to the potential imparted both to the film and to such gas in the ordinary "good" forming electrolytes.

In its action a so-called "good" forming electrolyte imparts a strong negative potential to the film, which means that as the oxide is formed it tends to strongly adhere to the anode surface. At the same time any gas formed will likewise have a strong negative potential and tends to stay in the pores of the film. Thus, when the voltage applied to a condenser provided with such a "good" electrolyte exceeds its critical voltage, breakdown through the gas bubble takes place and produces the deleterious results previously described.

With an electrode operated in accordance with our invention, the film has only a slight negative zeta potential. Furthermore, any gas formed during operation, having also a low negative potential, is liberated easily and freely and escapes from the film surface without such gas accumulating in the pores to form such previously described spark gaps and no sparking can take place.

Since the formation of a stable dielectric in an electrolyte which imparts to it a low zeta potential is extremely difficult no appreciable unhydrated film-formation will take place as contrasted to the formation in a "good" forming electrolyte as previously described. For this reason it is generally desirable to initially form the dielectric film on the electrode in one of the so-called "good" electrolytes.

The distinction between condensers of our invention and those of the prior art may be substantiated by observing the behavior of such condensers under pressure. In an ordinary condenser, increasing the external pressure on the electrolyte, increases the pressure on the gas in the pores of the film, and it can be readily observed that the sparking voltage of the condenser

increases. Conversely, lowering the pressure lowers the sparking voltage of the condenser. However, in both instances, sparking is present and may be readily seen.

In the condenser of our invention, there is no sparking, and increasing the pressure merely increases the leakage current. This is explained by the fact that under pressure, the electrolyte displaces the gas formed and permeates into the pores of the film thereby lowering its effective resistance.

The type of electrolyte found to impart the unique characteristics to the condenser of our invention is, as above stated, one which imparts a low negative potential to the film and to the gas formed at the surface of the electrode. We have found that the desired lowering of the potential may be obtained by increasing the concentration of the electrolyte, i. e. increasing the number of positive and negative ions available in the solution.

The potential produced by the electrolyte may also be controlled by varying its pH value and/or by proper selection of the ions made to exist in the solution.

A process suitable for the formation of electrolytic condensers having the aforesaid unique characteristics is described in detail in our copending application Ser. No. 743,468, filed September 10, 1934 now Patent No. 2,122,392. It should, however, be understood that the process of said application is not limited to the manufacture of the special condensers forming the subject matter of this application. On the other hand, these special condensers can be manufactured also by other processes, the general characteristics of which are that they produce a film which comprises adjacent to the aluminum a layer which is of substantially pure unhydrated oxide, and has a thickness corresponding to the critical voltage, and preferably also comprises an adjacent layer formed of a mixture of aluminum oxide and aluminum hydroxide or other compounds of aluminum. These processes, however, do not form a part of the present application.

In the process described in the application Ser. No. 743,468, the electrode or electrodes of the condensers are subjected to a two-step forming process, each forming step being a rapid formation step, as more fully described in the U. S. A. Patents No. 2,057,314 and No. 2,057,315 to Preston Robinson.

According to the process described in our above application, in the first forming step the electrode is formed in an alkaline electrolyte and in the second step in an acidic electrolyte. In the first step the formation takes place by immersing into the electrolyte successive unfiled portions of the electrode and applying thereto immediately the maximum forming voltage. This voltage, for instance, for condensers in which the critical voltage is to be 300 volts, will be about 300 volts, although under certain circumstances the forming voltage may vary to some extent from such critical voltage. In the second step, the forming voltage is preferably the same as in the first step, but it is not altogether necessary to gradually immerse the electrode as the electrode is already filmed. As a rule the second forming step requires about 15 to 30 minutes. This time, however, is not critical.

We shall describe our invention on hand of a specific example and in connection with a so-called wet electrolytic condenser for radio filter circuits, for which it is especially important.

However, it should be well understood that our invention is broadly applicable to various types of electrolytic condensers.

In the drawing forming part of the specification:

Figure 1 is a schematic diagram showing a filter circuit of a radio receiving set utilizing condensers of our invention;

Fig. 2 is a graph illustrating the voltage-leakage current characteristics of our novel condensers.

The filming electrode of the condenser consists of a suitable filming material, for instance of aluminum, tantalum, zirconium, etc. Aluminum, because of its good film-forming properties, easy workability, and low cost, is the most widely used filming metal, and we shall describe our invention with reference to aluminum electrodes.

As previously stated, a process suitable for the formation of electrolytic condensers in accordance with our invention, is described in detail in our copending application Ser. No. 743,468.

Both of the formation steps described in said application preferably, but not necessarily, take place before the assembly of the condensers, and usually a plurality of electrodes are formed simultaneously.

In the first forming step the electrode is immersed in an alkaline electrolyte which preferably comprises as ionogen an alkaline salt of a weak acid, for instance, borax, sodium-phosphate, etc. The solution used is preferably a very dilute aqueous solution of such ionogen. For condensers to be formed at 300 volts we may use, for instance, a solution comprising two ounces of borax to three gallons of water.

The electrodes are gradually immersed in the electrolyte with the immediate application of the full forming voltage, for example, 300 volts. Thereby, as has been fully described in the U. S. A. Patents No. 2,057,314 and No. 2,057,315 to Preston Robinson, the film forms almost instantaneously on successive unfiled portions of the electrode as they immerse into the electrolyte.

This formation takes place at extremely high current densities, which, together with the high voltage, causes an exceedingly high electrostatic equivalent pressure at the film and this high pressure and rapid formation forms a very dense and unhydrated oxide film on the electrode. The temperature of the forming bath in this step should not exceed about 50° C.

A specific characteristic of this forming step, as has been described in detail in our above said application, is that contrary to usual forming processes, there is no chemical reaction outside of the film formation, i. e., the usual production of reaction products in the electrolyte, for instances, of aluminum oxide and boric acid, is entirely absent.

The film formed in this step on the aluminum electrodes has minute pores. One of the purposes of the second formation step is to convert a portion of the dense unhydrated film into a film which is less dense, more fibroid and elastic which covers and/or fills such pores.

The second forming step consists in immersing the filmed electrodes into an acid electrolyte comprising, for instance, for 300 volt condensers, 70 1 lb. borax, 4 lbs. boric acid, 6 gals. water, the forming electrolyte preferably having a temperature of 80° C. or more. Again, the above-referred to rapid formation process is preferably used; other weak acids as phosphoric, citric, 75

tartaric acid with or without the addition of salts of a weak acid may also be used.

In this second forming step the aluminum oxide film reacts at its surfaces with the acidic constituent of the electrolyte.

The filming electrode so formed is then assembled into a condenser with a suitable electrolyte, usually an aqueous solution of a weak acid and/or the salt of a weak acid, whereby the salt of the weak acid does not need to be the salt of the acid used. Such weak acids are, for instance, boric acid, phosphoric acid, citric acid, tartaric acid, etc., and the salts used are generally alkaline metal or ammonium salts of such weak acids.

The electrolytes using such constituents are usually to be of fairly high concentration. For use with 300 volt condensers we have found the following composition to give excellent results:

Boric acid..... 127 grams per liter of water  
28% ammonia..... 22 ccs. per liter

This electrolyte has a low resistivity of the order of 50 ohms per centimeter cube at 25° C. and a pH is between 6.9 and 7.

Equally as suitable is an electrolyte composed of—

Boric acid..... 137 grams per liter of water  
Sodium hydroxide... 13 grams

The resistivity of this electrolyte is of the order of 85 ohms per centimeter cube at 25° C. and its pH is between 6.9 and 7.

The other electrode of the condenser may form the container and may be of aluminum or other filming or non-filming metal.

The advantages of our novel condenser will be described on hand of a typical example:

Figure 1 is a schematic circuit diagram of the power supply of a radio receiving set. The regular A. C. lighting current is transformed to the proper voltage and then rectified and filtered to supply the plate current for the tubes of the set. The rectifier 1 is shown as a full-wave rectifier, the input side of which is connected to the winding of the transformer 20.

The leads 10 and 11 supply the rectifier and smoothed current to the plate circuits of the tubes.

The filter system provided between the rectifier and the output consists of two choke coils 5 and 6, connected in series in lead 10 and of three condensers 2, 3, and 4. Of these condenser 2 is connected across leads 10 and 11 directly behind the rectifier; condenser 3 is connected across these leads between choke coils 5 and 6; and condenser 4 is connected across the leads 10 and 11 in the rear of choke coil 6. We shall consider primarily condensers 2 and 3.

The output or load of the rectifier which consists of the sum of the plate currents of the tubes of the radio set is in most of the sets of the order of 1000 milliamperes, whereas the normal output voltage is in normal operation usually 250 to 300 volts.

The inherent characteristics of the rectifiers most widely used are such, that their voltage output decreases with increasing load. For instance, in the normal vacuum type of rectifier tubes at zero load, the voltage output of the tube is about 450 to 500 volts, whereas at a load of 100 milliamperes it is about 250 to 300 volts.

As is well known, the plate current through the tubes of the set only starts to flow when the cathode of the respective tubes has been brought to their proper electron-emitting temperature.

In modern sets using indirectly-heated cathodes, the time required for the cathodes to attain their full electron-emitting temperature is usually of the order of 10 to 25 seconds. Consequently at the instant a radio receiving set is put in operation, practically no current flows through the rectifier and thus a high voltage is delivered by the rectifier tube and the same high voltage exists across the condenser 2.

For this reason, as has been previously more fully explained, the condensers used for this purpose, had in the past to be made for 450 to 500 volts, in spite of the fact that in normal operation they operate only at 250 to 300 volts.

On the other hand, condensers according to the invention, formed for 250 to 300 volts, can be employed for this purpose without any damaging of the condensers. Thereby initially when the set is switched on, a current of considerable magnitude flows through the condenser. For example, a 16 mfd. condenser formed according to our invention for 300 volts operation will draw a current of the order of 40-50 milliamperes at a voltage of about 400 volts, without localized breakdown of the dielectric film taking place.

After 10 to 25 seconds as the radio tubes assume their electron emitting temperature and plate current starts to flow, the rectifier load increases and its voltage as well as the voltage across the condenser is reduced to about 250 to 300 volts. Under these normal operating conditions the leakage current through the condenser decreases to its small normal operating value, which is of the order of a fraction of a milliampere.

In the specific example both condensers 2 and 3 have been formed for 350 volt operation, condenser 2 having 8 mfd. and condenser 3, 16 mfd. capacity. When the set is switched on a voltage of about 450 volts is applied across condenser 2 and passes therethrough a current of about 23 milliamperes, and a voltage of 410 volts is applied across condenser 3 and passes therethrough a current of about 40 milliamperes. Gradually the voltage across these condensers drops below 350 volts and as the voltage drops the leakage current drops down to a negligible value.

Fig. 2 shows the general shape of the curve of the leakage current as function of the voltage for a condenser formed at 300 volts according to our invention. As will be noted, at the "critical voltage" there is a sharp bend or knee in the curve. This "critical voltage", as has been stated before, however, does not need to be the forming voltage.

It should be well understood that our invention is not limited to wet electrolytic condensers, nor to condensers used in filter circuits, but can also be applied to so-called "dry" electrolytic condensers, as well as to A. C. condensers.

Therefore, we do not wish to be limited to the application and example described, but desire the appended claims to be construed as broadly as permissible in view of the prior art.

What we claim is:

1. An electrolytic condenser comprising a filmed electrode having an effective dielectric film formed at a maximum forming voltage of several hundred volts and adjacent to the surface of the electrode consisting of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode, said condenser when operated at voltages exceeding its critical voltage, not exhibiting sparking.

2. An electrolytic condenser comprising an aluminum electrode having an effective dielectric film formed at a maximum forming voltage of several hundred volts, said film adjacent to the surface of the electrode consisting of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode, said condenser when subjected to a voltage exceeding its critical voltage exhibiting a large increase in leakage current without accompanying sparking phenomenon.

3. An electrolytic condenser comprising a filmed electrode having an effective dielectric film formed at a maximum forming voltage of several hundred volts, said film consisting adjacent to the aluminum of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode, said condenser when operated at voltages exceeding its maximum forming voltage not exhibiting sparking.

4. An electrolytic condenser comprising an aluminum electrode having an effective dielectric film formed at a maximum forming voltage of the order of 250 to 350 volts, said film consisting adjacent to the aluminum of substantially unhydrated aluminum oxide, and an electrolyte comprising an aqueous solution of a weak acid and a salt of a weak acid, said electrolyte being incapable of forming an unhydrated film on the aluminum, said condenser having at a voltage exceeding said maximum forming voltage, a much increased leakage current and exhibiting no sparking.

5. An electrolytic condenser comprising a filmed electrode formed at a maximum voltage of the order of several hundred volts, said film adjacent to the surface of the electrode consisting of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode, said condenser being characterized by its lacking a sparking voltage.

6. An electrolytic condenser comprising an electrolyte and an aluminum electrode immersed in said electrolyte, said electrode provided with

a layer of substantially unhydrated aluminum oxide adjacent to the surface of the electrode and adjacent to said unhydrated aluminum oxide a layer of hydrated aluminum oxide effectively blocking the surfaces of said unhydrated layer, said electrolyte being incapable of forming an unhydrated film on the electrode, said condenser being adapted to operate at a greatly increased leakage current at a voltage exceeding that at which said electrode has been formed without exhibiting sparking.

7. In an electrolytic condenser, an aluminum electrode provided with a substantially unhydrated aluminum oxide film and an electrolyte which imparts a substantially zero negative zeta potential to said film.

8. An electrolytic condenser comprising an aluminum electrode having an effective dielectric film formed at a maximum forming voltage of the order of several hundred volts, said film consisting adjacent to the aluminum of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode and comprising a weak acid and a salt of a weak acid, said electrolyte having a resistivity of less than 250 ohms per centimeter cube at 25° C., said condenser having at a voltage exceeding said forming voltage a much increased leakage current and exhibiting no sparking.

9. An electrolytic condenser comprising an aluminum electrode having an effective dielectric film formed at a maximum forming voltage of the order of several hundred volts, said film consisting adjacent to the aluminum of substantially unhydrated aluminum oxide, and an electrolyte incapable of forming an unhydrated film on the electrode and comprising a weak acid and a salt of a weak acid, said electrolyte having a resistivity of less than 250 ohms per centimeter cube and a pH between 6.7 and 7.1 at 25° C., said condenser having at a voltage exceeding said forming voltage a much increased leakage current and exhibiting no sparking.

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