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## ELECTROLYTIC CONDENSERS

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**Summary.** This article discusses the characteristics of electrolytic condensers and outlines the principles of their operation. Different types of electrolytic condenser for a variety of duties are described.

### Introduction

It has been known for several decades that various metals, such as aluminium, tantalum, niobium, zirconium and titanium, can be coated with an oxide film by electrolytic means. This may be done by introducing the metal into a suitable electrolyte, for instance aluminium in a sodium phosphate solution, and passing a current through it, the metal forming the positive pole of the circuit (*fig. 1*). Oxygen is evolved at this pole and oxidises the metal.

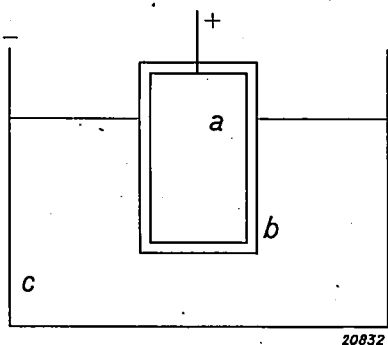


Fig. 1. Diagrammatic construction of an electrolytic condenser. *a* is the aluminium electrode, *b* the separating film of aluminium oxide, and *c* the electrolyte.

The thin film of oxide ( $\text{Al}_2\text{O}_3$ ) produced on aluminium offers a very high resistance to the further passage of the current, whose intensity therefore diminishes. If the applied voltage is kept constant the current through the system after a time tends towards a certain minimum value, termed the dissipating current. A cell of this type with aluminium as the positive electrode and an electrolyte as negative electrode can be used as a condenser,

the oxide film separating them acting as a very thin dielectric and thus making the resulting capacity comparatively high.

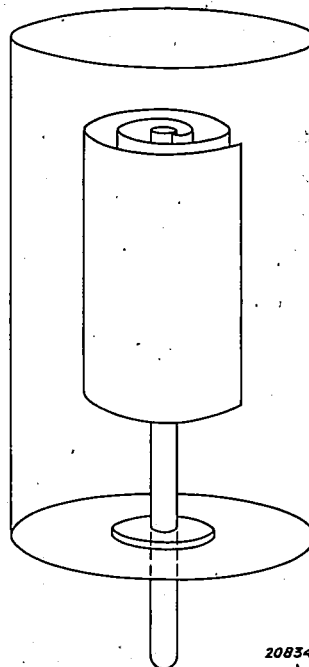


Fig. 2. Electrolytic condenser in which one of the electrodes consists of a spirally-coiled aluminium strip.

In the past it has not been found possible to reduce the dissipating current to such a low value that the heat evolved in the electrolyte could be neglected. The heat evolved was for instance 2 watts with a condenser containing approximately 50 c.c. of electrolyte, and through which a dissipa-

ting current of 0.01 A flowed at a potential difference of 200 volts. This signified the evolution of approximately 0.5 cal of heat per sec with a thermal capacity of 50 cals per degree, so that the temperature of a condenser of this construction was raised by about  $\frac{1}{2}$  degree per minute.

Only after the development of radio technology and as a result of researches in various industrial laboratories were suitable means discovered for sufficiently reducing the above-mentioned dissipating current, e.g. to below 1 mA.

About 1930 electrolytic condensers were introduced for radio purposes. These consisted of an aluminium plate of suitable shape which was covered with a very thin film of aluminium oxide. The aluminium electrode was surrounded by an electrolyte, usually boric acid with some added borate, and the complete condenser enclosed in a small container (fig. 2).

#### Characteristics of the Electrolytic Condenser

The different characteristics of the electrolytic condenser will first be reviewed.

The electrolytic condenser has a high capacity. The thickness  $d$  of the oxide film coating the aluminium is very thin (approximately  $10^{-5}$  cm), and the dielectric constant  $k$  of the  $\text{Al}_2\text{O}_3$  produced is high (about 10). Calculating the capacity  $c$  per sq. cm from these data, we get:

$$c = \frac{k}{4\pi d} = \frac{10}{12.6 \cdot 10^{-5}} = 8 \cdot 10^4 \text{ cm.}$$

For an aluminium electrode of 100 sq. cm surface a capacity of already approximately 8  $\mu\text{F}$  can thus be obtained. More detailed reference will be made below to the extent the thickness  $d$  of the oxide film depends on the potential employed when forming the condenser, i.e. when producing the oxide film.

The electrolytic condenser can only be employed with a flow of current in one direction. The aluminium electrode must always be connected to the positive side of the applied voltage, and the body of the condenser, i.e. the electrolyte, must therefore always be negative. With current flowing through the condenser in this direction, the current intensity is small; it appears as if the condenser has a slight leak and as if a high resistance were connected in parallel with the condenser. This resistance is determined by the potential. If the direction of current flow is reversed, a strong current will flow through the condenser and the latter becomes useless as such.

It is thus seen that the system exhibits the characteristics of a rectifier, and the condenser does

not then differ in any way from the well-known electrolytic rectifier.

As already indicated the condenser coatings consist of aluminium and electrolyte. The specific resistance of an electrolyte is, however, high as compared with that of metals (of the order of 100 ohms per cm). The condenser coating composed of electrolyte has therefore an appreciable resistance which is in series with the condenser.

If the potential difference applied to an ordinary type of condenser, for instance a mica condenser, is progressively raised a puncturing of the dielectric will result. What happens with an electrolytic condenser when the potential difference is similarly increased? If this difference between the aluminium and the electrolyte is steadily raised, a sparkover will be initiated between them at a certain voltage. The dissipating current, which already increased during the stepping up of the voltage, commences to rise much more rapidly when sparking begins. This sparking is analogous to the breakdown of the dielectric in an ordinary condenser, but with the fundamental difference that the flashover does not have destructive results in the case of the electrolytic condenser. The resulting disturbance of the dielectric is in fact instantaneously eliminated by the oxygen which is simultaneously evolved by the dissipating current.

Fig. 3 shows the diagrammatic circuits of an electrolytic condenser.  $C$  is a condenser of the same capacity as the electrolytic condenser. The condenser plate  $a$  represents the aluminium electrode, the dielectric  $O$  the film of aluminium oxide.  $b$  is the electrolyte whose resistance  $R$  is in series with the

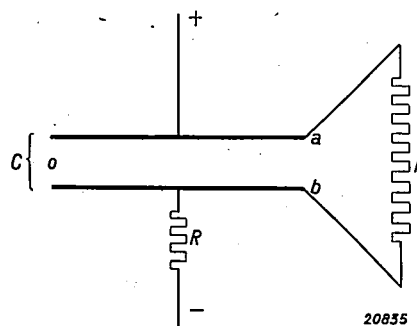


Fig. 3. Diagrammatic circuit of the electrolytic condenser.  $a$  is the aluminium electrode,  $O$  the oxide-film dielectric of the condenser  $C$ , and  $b$  the other electrode composed of electrolyte.  $r$  is the resistance of the separating layer in parallel with the capacity  $C$ ;  $R$  denotes the resistance of the electrolyte in series with the condenser  $C$ .

condenser. Between the condenser plates  $a$  and  $b$  there is a resistance  $r$  corresponding to the dissipating current and which diminishes with rising voltage.

As a rule the electrolytic condenser is employed in circuits in which a comparatively low alternating current is superimposed on the unidirectional current.

When considering this alternating current the resistance  $r$  can be neglected. The series resistance  $R$  is composed of the resistance of the electrolyte which is governed by the frequency, and a resistance which we may term the loss resistance in the oxide film. The losses in the oxide film increase with the frequency, the tangent of the phase difference of the oxide film (the resistance of the electrolyte thus being neglected) varying from approximately 2 per cent at 50 cycles to approximately 6 per cent at 1000 cycles. The capacity itself is practically independent of the frequency, and in the band from 50 to 1000 cycles it does not alter by more than 5 per cent.

### Explanation of Electrolytic Rectification

The difference in current transmissibility through the system Al — Al oxide film — electrolyte in the two directions may be accounted for as follows: We have already seen that the oxide film is very thin, being of the order of  $10^{-5}$  cm, so that if a potential difference of 100 volts is applied between the aluminium and the electrolyte, the field strength in the dielectric will be about  $10^7$  volts per cm. With such high field intensities, a "cold emission" always takes place, i.e. the negative electrode emits electrons.

Consider now two plane metal electrodes between which the field intensity  $F$  is so high that the negative electrode emits electrons; it is then found that the electron current  $i$  can be represented by an equation of the form:

$$i = AF^2 e^{-\frac{B}{F}}$$

where  $A$  and  $B$  are constants of the materials.

Assume that the plate  $a$  emits electrons more easily than plate  $b$ . This signifies that when an alternating voltage is applied the current passes through with greater facility in one half wave than in the other half, the greater current flowing when the plate more susceptible to electronic emission constitutes the negative pole.

To rectify a current a thin layer of insulation is therefore necessary and must be bounded by two substances capable of emitting electrons to very different degrees. If the substance which emits electrons the more easily is made negative, a higher current will flow than when it is positive.

Substances are indeed known which emit elec-

trons with different facilities and intensities; metals emit electrons easily, and semi-conductors and electrolytes emit them with difficulty. The electrons in the electrolyte are in fact not free but are linked to ions, although the powerful field obtaining can detach the electrons from the ions and transfer them to the separating layer.

It is thus seen why the electrolytic condenser must always be connected up in such a way that the electrolyte is the negative pole, for then only will a weak dissipating current flow through the condenser. It would be most desirable to have no dissipating current at all, but as we shall see later this is unavoidable. It also follows from the above that the dissipating current will be the lower, the smaller the number of ions present in the electrolyte, i.e. the less current it conducts.

Electrolytes with a high specific resistance actually exhibit low dissipating currents, but these electrolytes have the drawback that the resistance  $R$  (fig. 4) in series with the condenser is made very great.

A compromise therefore becomes imperative, and consists in fixing the permissible series resistance  $R$  and tolerating the corresponding dissipating current. Fortunately in this way very low dissipating currents (less than 1 mA for 450 volts at several  $\mu F$ ) have been realised.

It is now evident why it is impossible to use a metal as a second electrode in place of the electrolyte. In such case the separating layer (aluminium oxide film) would be bounded by two substances which emit electrons with almost the same facility, so that a high current would flow in both directions and the condenser be of no practical value. Moreover a breakdown of the dielectric would occur already at low voltages. The specified polarity and the use of an electrolyte are therefore indispensable requisites.

### Condensers for Different Voltage Ratings

We have already seen that the dissipating current is generated because the electrolyte is also able to emit electrons when a powerful electric field is applied to it, such electrons migrating through the oxide film to the aluminium. This current is determined by the field strength. If in condensers made of the same materials the dissipating currents are the same at equal potential differences, it may be concluded that the oxide films are of the same thickness. The field intensity is then equal to:

$$F = \frac{\text{applied voltage}}{\text{thickness of separating layer}} = \frac{V}{d}$$

If an aluminium electrode is oxidised in an electrolyte and a specific potential difference  $V_1$  is applied, then as already indicated at the outset the current through the electrolyte will steadily diminish. At a certain small terminal value  $i_1$  of this current, the oxidation process may be regarded as having terminated. If now a second aluminium electrode with the same dimensions is placed in the same electrolyte and a potential difference  $V_2$ , which is double  $V_1$ , is applied, and we wait until the dissipating current has attained the same final value  $i_1$ , it may then be assumed that in the two condensers the same field strength prevails at the separating film of the electrolyte. Since however  $V_2 = 2 V_1$ ,  $d_2$  must be  $2 d_1$  and hence also the capacity of the second condenser half as great as that of the first. With an anode rated for 500 volts the thickness of the oxide layer is  $0.6 \mu$ .

Thus with the same area of aluminium we can make a condenser with e.g. a rating of  $10 \mu\text{F}$  at 500 volts,  $20 \mu\text{F}$  at 250 volts,  $50 \mu\text{F}$  at 100 volts, etc. One of the principal advantages of the electrolytic condenser is that the thickness of its insulating layer is automatically matched to the potential difference.

### Disruptive Voltage of Electrolytic Condensers

Mention has already been made of the fact that sparking occurs with an electrolytic condenser when a certain critical potential difference is applied to it, such sparking being analogous to the breakdown of the dielectric in a standard condenser.

It is observed that this sparking voltage  $V$  is determined by the specific resistance ( $\rho$ ) of the electrolyte, and for a particular thickness of film is given by the expression:

$$V = a \log \rho + b$$

where  $a$  and  $b$  are constants.

The increase of  $V$  with  $\rho$  may be interpreted as follows: The greater the concentration of the ions in the electrolyte, the greater will be the current emanating from the electrolyte, and hence the greater the number of electrons migrating to the dielectric, and the easier will breakdown (sparking) develop.

Theoretically therefore condensers with a very high disruptive voltage can be produced by making the specific resistance  $\rho$  of the electrolyte sufficiently great. But the need for none too high a series resistance compels a compromise to be met, as already indicated when considering the dissipating current.

That the condenser does not suffer permanent

deterioration from sparking has already been indicated, and this is still the case when the applied over-voltage is very high. While in this case the dissipating current is indeed higher, it yet assumes its normal value again with a normal working voltage soon after being overloaded.

### Effect of Temperature on an Electrolytic Condenser

The temperature primarily affects the conductivity of the electrolyte, which rises with the temperature so that the series resistance  $R$  diminishes. With temperature increase the density of the free ions and their mobility also increase, resulting in an increase in the dissipating current. Between 20 and 60 °C this current becomes about three times greater, but is then still very small.

### Electrolytic Condenser in Use

It has already been stated that the dissipating current continuously generates oxygen at the anode, the gas producing oxidation. The oxide film hence becomes thicker during the use of the condenser and the capacity diminishes. This decrease is however extremely small, since the dissipating current is itself low. Condensers having a liberal rating of  $10 \mu\text{F}$ , after being in use for a year at 450 volts, have exhibited an average reduction in capacity of only  $0.8 \mu\text{F}$ . The dissipating current and the resistance also remain practically constant.

When an electrolytic condenser has been taken out of service for a period of a few months, a fairly high current will be found to flow through the condenser during the first few seconds a potential difference is applied to it. The dissipating current drops very rapidly however, becoming small after a few minutes, and shortly after regains the value which it had when the condenser was taken off load.

### Construction of Electrolytic Condensers

The electrolytic condensers made by Philips may be conveniently divided into three main groups differing from each other in construction as well as in their working voltage rating.

The most common type in use, which is termed the star type from the shape of the anode, is made for working voltages of 320, 350 and 450 volts. For working voltages of 500 and 550 volts a special high-tension type of condenser is made, while the so-called low-tension type is designed for working voltages of 25 and 12.5 volts. Details of these different types are given below, as well as some considerations which determined their specific designs.



1) Star Type (Fig. 4)

The anode in this condenser consists of a star-shaped aluminium electrode combining a large

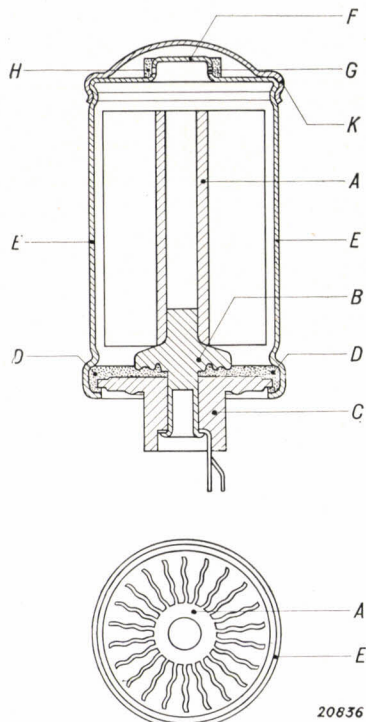


Fig. 4. Construction of a star-type electrolytic condenser. The anode *A* consists of a star-shaped aluminium rod. By means of the pin *B* the anode is rigidly connected with the "Philite" plug *C* which is threaded. The rubber gasket *D* provides a liquid-tight seal between the anode and the "Philite" plug and between the plug and the aluminium case (cathode). The aluminium sleeve *E* contains a valve at the top consisting of the bell-shaped extension *F* in the projecting wall of which holes *G* have been drilled. These holes are closed by the surrounding rubber band *H*. If the pressure in the condenser rises too far, pressure relief is obtained through the holes *G* along the rubber band *H*. The whole assembly is closed with the aluminium cap *K* which contains an absorbent material to take up any liquid trickling out of the valve. The sleeve is filled with electrolyte up to the edge of the anode.

surface with a small volume. A method was developed in the laboratory for increasing the surface of the aluminium by chemical means (etching), as shown in *fig. 5*. By this etching process the initially smooth surface was roughened to such an extent that the active surface was enlarged several times. If aluminium treated in this way is prepared in the usual way, a capacity is obtained which on the average is seven times greater than that with a smooth surface. To this the compact dimensions of these condensers are due.

The condenser case which also acts as the cathode consists of an aluminium cylinder closed at the bottom by a threaded "Philite" plug. This plug also serves for fixing the condenser and as an insulator for passing through the anode to the anode

terminal. A rubber gasket giving a perfectly liquid-proof seal is inserted between the aluminium



Fig. 5. Photograph of an etched electrode surface.

case and the "Philite" plug. The whole is filled with electrolyte of specific composition which differs according to the voltage rating. A valve is situated in the top of the aluminium case to allow the escape of gases evolved during service. It opens with an excess pressure less than 1 atmosphere. An absorbent mass is plugged round the valve to absorb any liquid trickling out through the valve, e.g. on high overloads; the whole assembly is closed by a cap.

The following table gives the principal data relating to this type of condenser.

Table I			
Capacity . . . . .	8	16	32 $\mu$ F
Max. working voltage . .	450	450	320 volts
Peak voltage . . . . .	480	480	350 volts
Series resistance at 50 cycles and 20 $^{\circ}$ C. . . . .	ab. 70	ab. 45	ab. 10 $\Omega$
Max. permissible alternating voltage at 50 cycles . .	23	23	16 volts
Max. dissipating current .	0.8	1.6	2 mA
Height . . . . .	49	69	69 mm
Diameter . . . . .	40	40	40 mm
Weight . . . . .	90	125	125 g
Max. working temperature	60	60	60 $^{\circ}$ C

For this type of condenser the dissipating current is plotted against the potential difference in *fig. 6*. Since electrolytic condensers are mainly used to eliminate any A.C. component present in a unidirectional voltage (voltage smoothing in radio apparatus) the maximum permissible alternating voltage is also given in the above table. Care must be taken that in every case the direct voltage simultaneously applied is always greater than the amplitude of the alternating voltage, in other words the anode must never become negative with

respect to the cathode. The working voltage in the table represents the sum of the applied direct

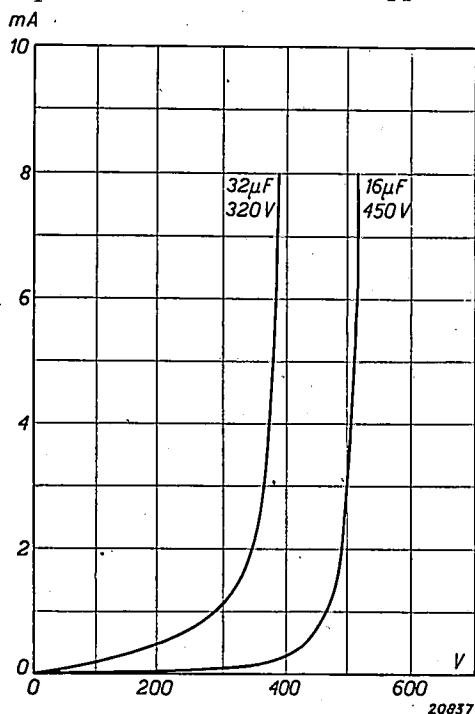


Fig. 6. Dissipating current of an electrolytic condenser plotted as a function of the voltage.

voltage and the amplitude of the alternating voltage. The peak voltage is the voltage which can be safely applied to the condenser for short periods. It should be noted why an electrolytic condenser cannot sustain alternating voltages of unlimited magnitude. The alternating current flowing through the condenser makes the cathode, which is also of aluminium, alternately positive and negative with respect to the electrolyte. As already indicated above the aluminium becomes covered with an oxide film when it is positive with respect to the electrolyte. As a result this alternating current produces a capacity also at the cathode; this capacity is in fact very high, but as it is in series with the anode capacity it may reduce the total capacity. Experiments have shown that with an alternating current density of 0.5 mA per sq. cm (at 50 to 100 cycles) the cathode capacity remains so high after several thousand hours' service that no appreciable diminution of capacity takes place. By submitting the aluminium used for the cathode to special treatment it has been found possible to raise the permissible alternating current to from 4 to 5 mA per sq. cm (at 50 to 100 cycles). It may be noted that oxidation of the cathode ceases at frequencies above 500 cycles.

For this condenser type fig. 7 shows the tangent of the phase difference ( $\tan \delta$ ) at 50 cycles as a function of the temperature from  $-10^\circ\text{C}$  to

$60^\circ\text{C}$ . The decrease in  $\tan \delta$ , or what is the same thing the drop in the series resistance, is due to the diminution of the specific resistance of the electrolyte with rising temperature. The dielectric losses in the separating layer are very small and can therefore be neglected in this connection.

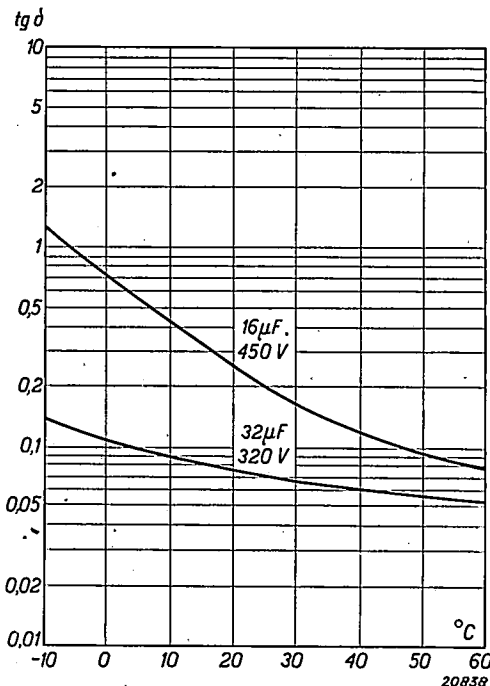


Fig. 7. Tangent of the phase difference ( $\tan \delta$ ) at 50 cycles as a function of the temperature.

## 2) High-Tension Type

For working voltages of 500 volts and over, electrolytes must be used with a fairly high specific resistance (approximately 10 000 ohms per cm at  $20^\circ\text{C}$ ). An  $8\ \mu\text{F}$  condenser of the star-type would thus give a series resistance of 300 ohms and over, which is far too high. The only means available for reducing the series resistance is to make the distance between the anode and the cathode as small as possible, as has been done in the high-tension type of condenser (see fig. 9). The anode, which is a die casting, here consists of an aluminium cylinder which is surrounded internally and externally by the cathode placed at a distance of approximately 1 mm. The characteristics of this type of condenser are given in the following table.

Tabel II.

Capacity . . . . .	8	$8\ \mu\text{F}$
Max. working voltage . . . . .	500	500 volts
Peak voltage . . . . .	550	600 volts
Series resistance at 50 cycles, $20^\circ\text{C}$ . .	ab. 40	ab. 60 $\Omega$
Max. A. C. Rating, 50 cycles . . . . .	30	30 volt
Max. dissipating current . . . . .	2	2 mA
Height . . . . .	112	112 mm
Diameter . . . . .	40	40 mm
Weight . . . . .	115	117 g
Max. working temperature . . . . .	50	$50^\circ\text{C}$

3) Low-Tension Type

These condensers are of similar construction to paper condensers; a cathode and an anode of thin aluminium foil are coiled together, being separated by a layer of paper impregnated with electrolyte, and enclosed in a compressed paper container; the two ends of the coil are compound sealed. The characteristics of this condenser are given in the following table:

Table III.

Capacity . . . . .	25	50 $\mu$ F
Working voltage . . . . .	25	12.5 volts
Series resistance, 20 °C . . . . .	ab. 6	ab. 6 $\Omega$
Max. A.C. rating, 50 cycles . . . . .	6	3 volts
Max. dissipating current . . . . .	50	50 $\mu$ A
Diameter . . . . .	17	17 mm
Length . . . . .	53	53 mm
Weight . . . . .	14	14 g

Comparison between Electrolytic and Paper Condensers

The advantages offered by the electrolytic condenser over the paper condenser are as follows:

- 1) Higher capacity per unit of volume, especially at low working voltages; the oxide film can be made very thin by employing lower voltages during surface oxidation, while in the paper condensers a minimum thickness of paper is imperative.
- 2) While in the paper condenser surges may result in a breakdown of the dielectric and hence the complete destruction of the condenser, the electrolytic condenser can sustain overloads without damage, any disturbance being automatically made good.

The advantages of the paper condenser over the electrolytic condenser are the following:

- 1) No continuous e.m.f. for polarisation is required, so that there is no dissipating current.

- 2) Only the paper condenser can be used for a pure alternating current load.

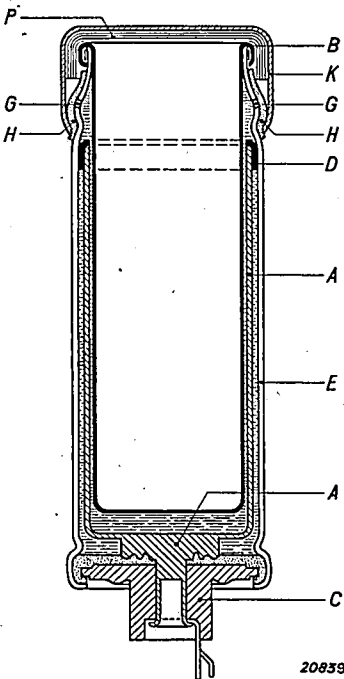


Fig. 8. Construction of a high-tension type of electrolytic condenser. The anode is a die casting and is shaped like an aluminium beaker closed at the bottom with the "Philite" plug C similar to that used in the star type of condenser. The cathode is made in two parts: one part constitutes the outer case of the condenser E, and the other an inner sleeve lapped at B to make liquid-proof contact with E. By adopting this construction the distance between the anode and the cathode is made very small. A strip of insulating material is fixed at D to facilitate the centering of the anode in the outer case during assembly. The valve again consists of a series of holes G in the outer container which are covered by a rubber band H. The valve is separated from the cap K by an intermediate layer of an absorbent material P.

- 3) The losses ( $\tan \delta$ ) in the paper condenser are smaller than the electrolytic condenser, particularly at high frequencies.
- 4) For low capacity ratings (below 2  $\mu$ F) the paper condenser is usually much cheaper than the electrolytic condenser.

In selecting a condenser for a specific duty these relative advantages and disadvantages must naturally be given careful consideration.