

March 19, 1940.

C. A. KOTTERMAN

2,194,182

RECTIFIER

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Fig. 1

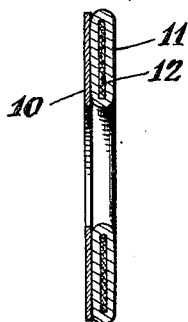


Fig. 2

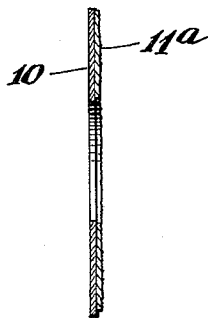


Fig. 3

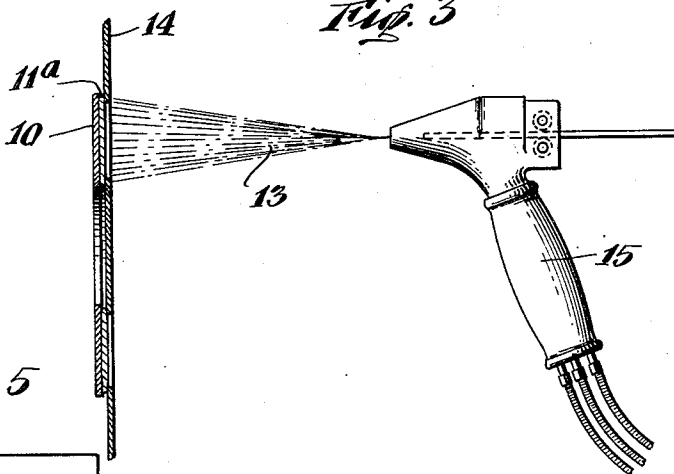


Fig. 5

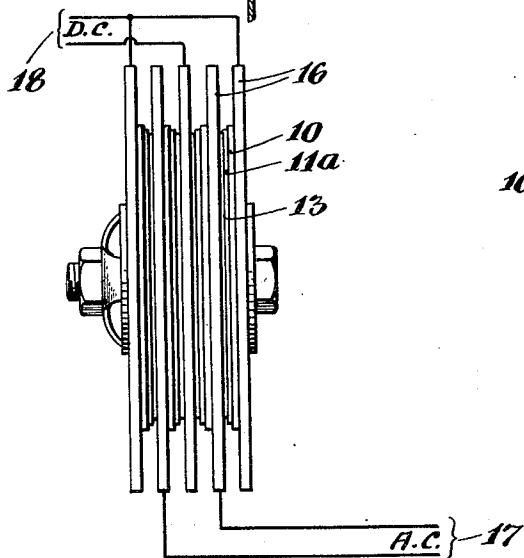
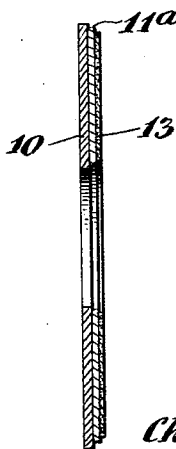


Fig. 4



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2,194,182

RECTIFIER

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Application July 13, 1939, Serial No. 284,145

10 Claims. (Cl. 175-366)

This invention relates to electric current rectifiers of the type comprising asymmetrically conductive couples of the dry surface contact variety.

5 An object of the invention is to improve such rectifiers and the method of making them.

Other objects of the invention will be apparent from the following description and accompanying drawing taken in connection with the appended

10 claims.

The invention comprises the features of construction, combination of elements, arrangement of parts, and methods of manufacture and operation referred to above or which will be brought

15 out and exemplified in the disclosure hereinafter set forth, including the illustrations in the drawing.

In the drawing:

20 Figure 1 is a cross section through an asymmetrically conductive rectifier couple;

Figure 2 represents the couple after further processing according to one aspect of my invention;

25 Figure 3 illustrates a further step in forming a finished rectifier;

Figure 4 shows a rectifier element after the process of Figure 3; and

Figure 5 shows a completed rectifier device.

30 A feature of my invention resides in the method of production of a thin rectifier element and the product of such method. Another feature resides in the electrical, chemical and mechanical treatment of the thin element to improve its characteristics. Still other features will be made

35 apparent in the following detailed description.

40 While a preferred embodiment of the invention is described herein, it is contemplated that considerable variation may be made in the method of procedure and the construction of parts without departing from the spirit of the invention. In the following description and in the claims, parts will be identified by specific means for convenience, but they are intended to be as generic in their application to similar parts as

45 the art will permit.

50 My invention has particular application to rectifiers of the dry surface contact variety such as are described in Samuel Ruben Patents 1,751,359; 1,751,361; 1,751,469 et al., and may comprise, for example, a layer of magnesium or zinc and a layer of cupric sulfide separated by a thin asymmetrically conductive layer resulting from the reaction of these two layers and comprising a film of magnesium sulfide.

55 Figure 1 shows such a rectifier couple produced,

for example, in the following manner; A brass washer is heated in the presence of sulfur in a non-oxidizing atmosphere until the copper in the brass has been converted into a hard dense body of sulfides. It appears that during sulfiding the zinc migrates to the center of the disc forming a core 12 predominantly of zinc sulfide surrounded by a copper sulfide shell 11 as shown in Figure 1.

A washer 10 of highly electro-positive metals; such as magnesium or zinc is provided with a thin insulating film on its surface by chemical or electro-chemical treatment and is then pressed into intimate contact with the insulated side facing the cupric sulfide washer which has previously been ground to a smooth flat surface. An alternating current of sufficient voltage to break down the insulating film is then applied across the junction. Upon breakdown of the insulating film a chemical reaction takes place resulting in the production of the asymmetrically conducting layer or rectifying film. The alternating current may be applied for a period sufficient to produce this rectifying film over substantially the entire junction area. The reaction also results in a strong bond being formed between the respective layers welding them strongly together.

According to one feature of my invention after the rectifying junction is produced resulting in the integral assembly shown in Figure 1 the magnesium or zinc washer 10 is peeled or stripped away from the main body of the cupric sulfide washer 11. If the electrical formation step has been properly regulated the rectifying film will completely adhere to the electro-positive metal and will carry with it a thin outer layer 11a of cupric sulfide as shown in Figure 2. Thus all the essential parts of the rectifying couple adhere to the magnesium or zinc washer and retain the same rectifying characteristics they possessed before the peeling operation.

The peeled rectifier junctions of my invention present important advantages over ordinary couples, for example;

A. They are flexible to the extent that they can be bent to a 90 degree angle then flattened out without destroying the rectifier properties. This feature permits them to be unevenly stacked, that is, it is not necessary to go to extreme limits in having all surfaces flat and parallel as in the stacking of the ordinary junctions where spacer washers, radiator and terminal plates and other components should have as flat register as is possible in stacking up a plurality of junctions on a common bolt.

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B. By separating the junction from the mother cupric, the possibility of failure due to cracked or fractured cupric sulfide washers is eliminated.

C. In the usual method of manufacturing cupric sulphide, brass washers are sulfided, converting the copper in the brass to cuprous sulfide and cupric sulfide, the zinc being converted into zinc sulfide. A zinc sulfide core is formed surrounded by cuprous and cupric sulfide. Zinc sulfide has a higher electrical resistance than cupric and cuprous sulfide. The peeling operation eliminates the zinc sulfide core and gives a thinner cupric sulfide layer of lower ohmic resistance.

D. Electrical conduction in the ordinary type of cupric sulfide washer having a core of any material other than a copper compound takes place mainly through the cupric sulfide shell. In the peeler type, conduction is through the entire body of the layer and consists of many parallel paths, removing the concentration of current at the edges of the junction and distributing it uniformly over the rectifying area of the junction resulting in an improved current ratio between the A. C. input current to the D. C. output current.

E. A peeled junction allows visible inspection of the completeness of formation of the rectifying film. Sensitive electrical tests have been developed for determining the completeness of formation for the ordinary type but they are more complicated and less reliable.

F. The peeled surface of the mother cupric sulfide washer can be reground flat and another rectifying film formed on the new surface. In this way at least four peeled rectifying junctions can be produced from one mother cupric using both sides, thereby effecting considerable economy in manufacture.

According to another aspect of my invention, and illustrating another advantage of the peeled rectifier junctions, I contemplate an additional treatment of the peeled junctions to improve their chemical and electrical properties.

During the original electrical formation of the magnesium or zinc sulfide rectifying film certain by-products are formed at the junction area which are not desired and which reduce the efficiency and other desirable characteristics of the rectifier. These are principally excess cuprous sulfide, copper oxide and metallic copper.

An excess of metallic copper raises the inverse current as well as the conducting current of the junction. This results in a lower DC/AC ratio.

An excess of cuprous sulfide in the rectifying film increases the IR drop in the conducting direction at high current densities. This lowers the DC/AC voltage ratio and hence lowers efficiency. An excess of cuprous sulfide also affects the shelf life of the rectifier causing the rectifier to lose its rectifying ability partially after a period of non-use. Normal rectification can only be restored by a high current treatment.

Copper oxide is detrimental since it reacts with sulfur producing free copper at the junction.

By additional treatment of the peeled junction it is possible to eliminate these detrimental products. This treatment comprises subjecting the peeled junction to the action of boiling sulfur or sulfur vapor. The sulfur penetrates the thin outer layer of cupric sulfide and reacts with the free copper, cuprous sulfide and copper oxide to convert them to cupric sulfide.

It will readily be apparent that if the junction had not been peeled off the mother cupric sulfide washer the resulfiding would be almost impossible

due to the thick layer of cupric sulfide which would have to be penetrated.

It is desirable to repeat the rectifier film-forming operation after resulfiding by passing an alternating current of suitable value through the junction.

The electrical characteristics of rectifiers made up of peeled junctions are considerably better than those normally obtained with rectifiers of standard construction.

The average inverse or blocking current of a magnesium cupric sulfide junction having a rectifying area of 1.7 sq. in. is 1.0-2.0 amperes when 6 volts D. C. are impressed across the junction with an 0.5 ohm current limiting resistor in series with the 6 volt supply. A junction having an area of 0.7 sq. in. has an inverse current of 0.5-0.75 ampere when 6 volts are impressed across the junction. When junctions of these areas are peeled, then subjected to the resulfiding process, the blocking current of the larger junction is reduced to between 80 and 100 milliamperes and that of the smaller junction to less than 50 milliamperes. This low inverse current greatly improves the peeled type of magnesium or zinc cupric sulfide rectifier for use in the low current field where high inverse currents could not be tolerated.

The usual thick type of magnesium or zinc cupric sulfide junction will stand an A. C. voltage of 3.5 volts RMS on load without junction instability. By peeling, then resulfiding and reforming, it is possible to raise this voltage to 4.0 volts RMS or higher on load retaining stability, a highly desirable advantage.

The current ratio of the peeled type junction shows a considerable gain over the conventional type. In three-phase, full-wave bridge operation, the peeled type frequently shows a current ratio of 1.2-1.3 whereas the conventional type in the same circuit lies between 1.1 and 1.15. The increased operating voltage per junction plus the improved current ratio is reflected in a higher efficiency of the peeled type. The peeled rectifier in three-phase, full-wave, 60 cycle operation working into a resistance or battery load will show an efficiency between 55 and 60%. At frequencies higher than 60 cycles, say, 300 to 3000 cycles, where the conducting cycle is of much shorter duration, the peeled rectifiers can be operated at 4.5-5.0 volts per junction.

In order to make good electric contact with the cupric sulfide layer 11a in the rectifier assembly the layer may be sprayed with a contacting metal, such as tin, nickel or other metal not readily sulfided. The peeled sulfide surface being rough affords an excellent surface for receiving a metal spray. The sprayed metal fills the minute depressions in the sulfide surface and forms a continuous layer over the surface.

Figure 3 shows the method of spraying cupric sulfide surface 11a with contacting metal 13 by use of a metallizing gun 15 and a suitable mask 14 to protect the edges of the junction.

Figure 4 illustrates the sprayed disc ready for assembly in a rectifying device.

Figure 5 shows a completed rectifying device made up of the elements of Figure 4 clamped together with heat-radiating and terminal plates 16, two of which are connected to an A. C. source 17 and the other three of which are connected to a D. C. output circuit 18 in the well-known full-wave bridge as shown. The soft contacting metal 13, such as tin, tends to flow slightly under the pressure of the stack and thereby

conforms itself to the adjacent surfaces and produces an improved contact.

The magnesium or zinc cupric sulfide rectifier requires a certain reservoir of cupric sulfide for maximum operating life. When the junction is peeled from the mother cupric washer only a thin layer of cupric sulfide adheres to the junction, usually a layer about .002 to .005 inch thick. While this will be sufficient in many cases it will be desirable for heavy current uses to build up the cupric sulfide layer of the peeled unit by spraying the layer 11a with metallic copper and then resulfiding the sprayed junctions to produce additional cupric sulfide. The cupric sulfide layer may thus be built up to a thickness in the order of 0.02-0.03 inch or greater, such as to 0.5 inch. The spraying operation is similar to that illustrated in Figure 3, using copper as the sprayed metal. Spraying with copper and resulfiding is, of course, accomplished before spraying with a contacting metal such as tin.

It is also possible to spray or otherwise apply a solution of cupric sulfide, such as cupric sulfide in alcohol, to the surface and then drying and resulfiding.

While the present invention, as to its objects and advantages, has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. An electric current rectifier comprising a layer of metal selected from the group consisting of magnesium and zinc, a layer of cupric sulfide and an interposed rectifying film produced by reaction therebetween, said layer of cupric sulfide having a thickness not substantially greater than 0.05 inch.

2. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer.

3. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then bringing the thin cupric sulfide layer into contact with sulfur at an elevated temperature.

4. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then depositing additional cupric sulfide on said thin layer of cupric sulfide.

5. The method of making a rectifying element which comprises placing a layer of a highly elec-

tropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then bringing the thin cupric sulfide layer into contact with sulfur at an elevated temperature and again passing electric current through the junction of said layer to reform the rectifying film thereat.

6. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer, depositing metallic copper on said thin layer of cupric sulfide and then sulfiding said deposited copper to produce additional cupric sulfide.

7. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then depositing an adhering metallic layer on said thin layer of cupric sulfide.

8. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then depositing an adhering layer of contacting metal on said thin layer of cupric sulfide.

9. The method of making a rectifying element which comprises placing a layer of a highly electropositive metal against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said electropositive metal layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer and then bringing the thin cupric sulfide layer into contact with sulfur at an elevated temperature and then depositing an adhering layer of contacting metal on said layer of cupric sulfide.

10. The method of making a rectifying element which comprises placing a layer of metal selected from the group consisting of magnesium and zinc, against a layer of cupric sulfide, passing an electric current through the junction of said layers to form a rectifying film thereat resulting from the reaction of said layers, and then peeling said magnesium or zinc layer together with said rectifying film and a thin layer of cupric sulfide from the main body of said cupric sulfide layer.

CERTIFICATE OF CORRECTION.

Patent No. 2,194,182.

March 19, 1910.

CHESTER A. KOTTERMAN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 14, for "supric" read cupric; line 16, for "0.5" read 0.05; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of April, A. D. 1910.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.