STUDIES IN CONTACT RECTIFICATION. II. THE CUPRIC SULFIDE-MAGNESIUM JUNCTION*

By Milton Bergstein, J. F. Rinke, and C. M. Gutheil
Research Laboratory, P. R. Mallory and Co., Inc., Indianapolis, Ind.

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Abstract

The commercial cupric sulfide magnesium junction consists of a disk of heat-treated, compressed cupric sulfide powder contacted under pressure with the suitably oxidized face of a magnesium disk. This rectifier is of the non-integral class and of the sulfide group. Oscillographic evidence indicates the formation of a film which possesses relatively high resistance to current flow from the magnesium to the cupric disk, slow partial destruction of the film on continued current flow in the opposite (low resistance) direction and "reformation" of the film within 0.004 sec when sufficient voltage is applied to send a current in the high resistance direction. Similar evidence indicates that there is no battery or thermoelectric effect within the junction of sufficient magnitude to account for rectification and that film "formation" and "destruction" are consequently electrothermic rather than electrolytic in origin. The phenomenon of "reverse rectification" is described. It is related to the a.c. voltage across the junction. Preliminary results for the relationship between efficiency and operating temperature of a bridge-type unit are in qualitative agreement with the theories which require film formation.

Introduction

A CONTACT rectifier is a device composed of dry dissimilar solids in good electrical contact through which current flows readily in one direction but not in the other. Contact detectors are of this class. They are merely small-current rectifiers. Rectifiers of the cupric sulfide-magnesium type and of the copper oxide-copper type are in commercial use for the rectification of large current at low voltages (usually below 120 volts). A cupric sulfide-magnesium rectifier unit of the bridge type may be made to output anywhere from 1 to 10 amperes d.c. using junctions of 0.515 sq. in. available area none of which are operated in parallel. The number of junctions used depends on the output voltage desired. The current density is higher in this type unit than in any other known commercial contact rectifier.

In a previous paper one of the authors[1] has divided rectifying junctions into general divisions according to mechanical structure and chemical constitution of the electro-negative member and has indicated what phenomena any accepted theory of contact rectification must at least qualitatively explain. Various fundamental mathematical theories[2] as well as

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[1] M. Bergstein, Trans. Am. Electrochem. Soc. **57**, Reprint 19 (1930)

[2] W. Schottky, Zeits. f. Physik **14**, 63 (1923), I. Stransky, Zeits. Phys. Chem. **113**, 131 (1925); R. Audubert and M. Quintin, Compt. rend. **188**, 52 (1929).

symbols of a more mechanical nature[3] have been used to explain contact rectification. These latter depend on an analogy between contact rectifiers and electron tubes. The first theories proposed were based on a supposed thermoelectric or battery effect at the rectifying junction. These have been subjected to some criticism.[4] Flowers[5] favored a theory that a blocking film was alternately formed and destroyed on each half cycle and Goddard's[6] experiments led him to the conclusion, in anticipation of the theories of Ruben and of Slepian,[3] that film formation of some kind is a necessary corollary of contact rectification.

In work on the cupric sulfide-magnesium rectifier it became necessary to establish whether film formation within the junction between the members actually did take place, under what conditions, and in what time. The results of this investigation, and other previously unstudied phenomena of this rectifier junction also, are reported herein.

According to the classification already referred to,[1] the cupric sulfide-magnesium rectifier is of the non-integral class and the sulfide group.

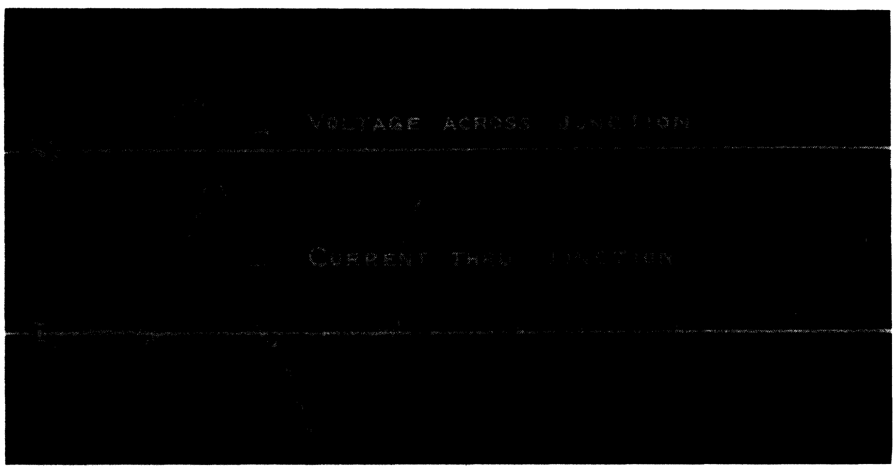


Fig. 1. Initiation of rectification.

Experimental

Nature of the rectifying junction. *Cupric sulfide disk.* The cupric sulfide disk (approximately 0.515 sq. in. in area) is prepared from compressed cupric sulfide powder which is subsequently heat treated to give a hard glassy mass and finally surface-ground to obtain a smooth finish.

[3] S. Ruben, U. S. Pat. 1,751,361 (1930) (filed 1925), L. O. Grondahl, Science **64,** 306 (1926), J. Am. Inst. Elec. Eng. **46,** 215 (1927); J. Slepian, Trans. Am. Electrochem. Soc. **54,** 201 (1928).

[4] F. Braun, Pogg. Ann. **153,** 566 (1874), Wied. Ann. **1,** 95 (1877); **4,** 476 (1878); G. W. Pierce, Phys. Rev. **29,** 478 (1909); Electrician **64,** 425 (1910).

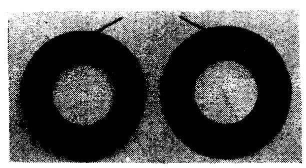
[5] A. E. Flowers, Phys. Rev. **29,** 445 (1909).

[6] R. H. Goddard, Phys. Rev. **34,** 423 (1912).

Particular care is taken in the heat treatment process to keep well below the dissociation temperature of cupric sulfide.

Magnesium disk. Pure magnesium strip of commerce is cleaned and mildly oxidized on the surface by one of a number of suitable processes either chemical or electrolytic. The nature of the oxidizing process is immaterial to this paper provided that a complete coat not so thick as to be too highly resistant be put on. The magnesium strip is subsequently cleaned on one face and punched into disks.

The junction. The oxidized surface of the magnesium disk is then contacted with one surface of the cupric sulfide disk and the two disks locked



CuS Mg
Fig. 2. Spots of adhesion.

together in a small vise under a pressure of several thousand pounds. The force required depends on the thickness of the oxide coat. When about 4 volts a.c. is applied to such a junction it attains rectifying properties in about the first four cycles as shown in the oscillogram of Fig. 1.

The direction of free passage of current is from cupric sulfide to magnesium. If the junction should now be removed from the vise, it is found

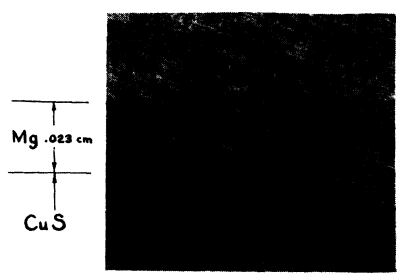


Fig. 3. Cross section of contact spot.

that the two disks are adherent and that the junction now has rectifying properties in spite of the removal of the pressure. If the two disks are pried apart, it is found that adhesion has occurred usually over a very small area. This is illustrated in Fig. 2 in which the points of adhesion on magnesium and cupric sulfide disks from the same junction are shown. If two such disks are again contacted with each other without the application of pressure, it is found that the junction is highly resistant and does not rectify. However, if pressure and voltage be applied as before, reformation takes place usually at some others pot. In the adhesion between the two disks actual fusion takes place. As indicated in Fig. 3 the structures of both the magnesium and the cupric sulfide are considerably changed at the contact spot. We have shown that this spot is the only place where current flow actually takes place. The simple expedient employed was to cover all of the oxidized magnesium surface except one tiny spot with a coating of insulating varnish. A very small piece of lead was placed on the magnesium behind the clear

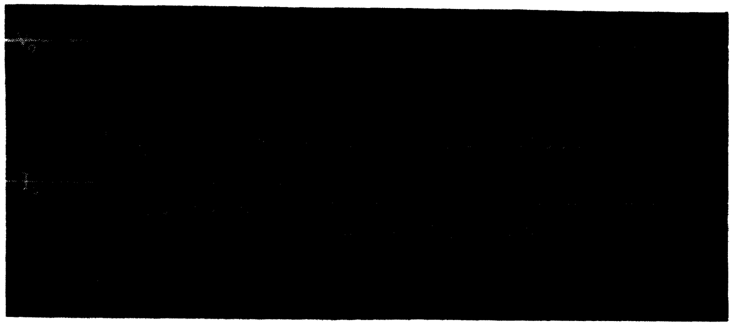


Fig. 4. d.c. formation of junction.

spot and the whole placed in a vise and assembled with a cupric sulfide disk as indicated above. The purpose of the lead was merely to deform the disk at the desired contact point and thus to effect contact with the cupric sulfide disk, which would have otherwise been separated from the magnesium disk by the thickness of the layer of varnish. It was found that a

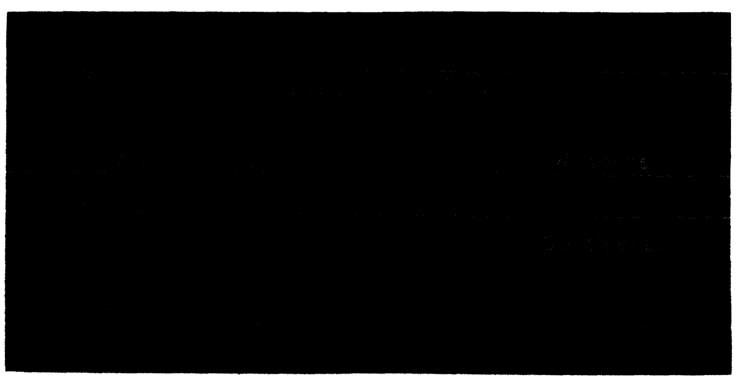


Fig. 5. Interruption in high resistance direction.

junction prepared in this way possessed substantially the same electrical characteristics as one prepared according to the standard practice thus establishing the fact that all the rectification and current flow takes place in the region of integral contact.

The film. Ruben[3] has pointed out that the energy required for this "fusion" probably results from the I^2R loss in the oxide coating and that the reaction results in the formation of a film to whose properties the behavior of the rectifier can be ascribed. Without examining any of the theoretical concepts involved we will here review the evidence we have accumulated indicating film formation.

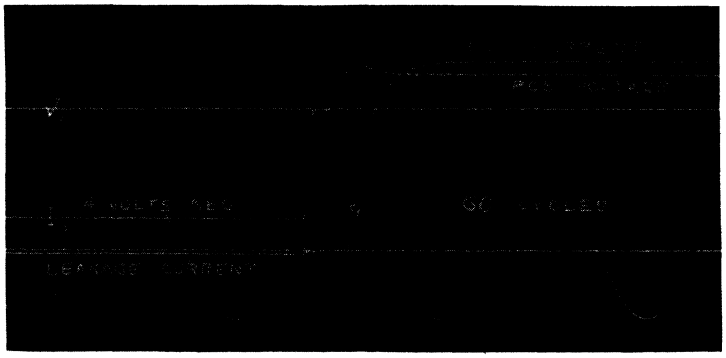


Fig. 6. Interruption in high resistance direction and reversal.

If, instead of applying a.c. to the unformed junction, approximately 4 volts d.c. is applied in the direction magnesium to cupric sulfide, the junction immediately becomes highly resistant in this direction and behaves as

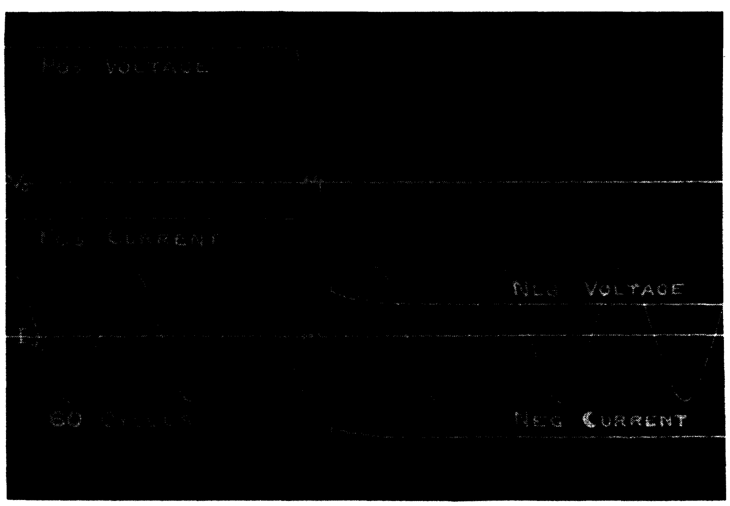


Fig. 7. Interruption in high resistance direction and reversal for cupric sulfide disk alone.

a normal rectifier when subsequently placed on a.c. The oscillogram of the development of this high resistance is shown in Fig. 4. Here we can observe that the resistance is initially extremely low but that in a period of approximately 0.02 sec. it increases to a value of the order of the final resistance in that direction.

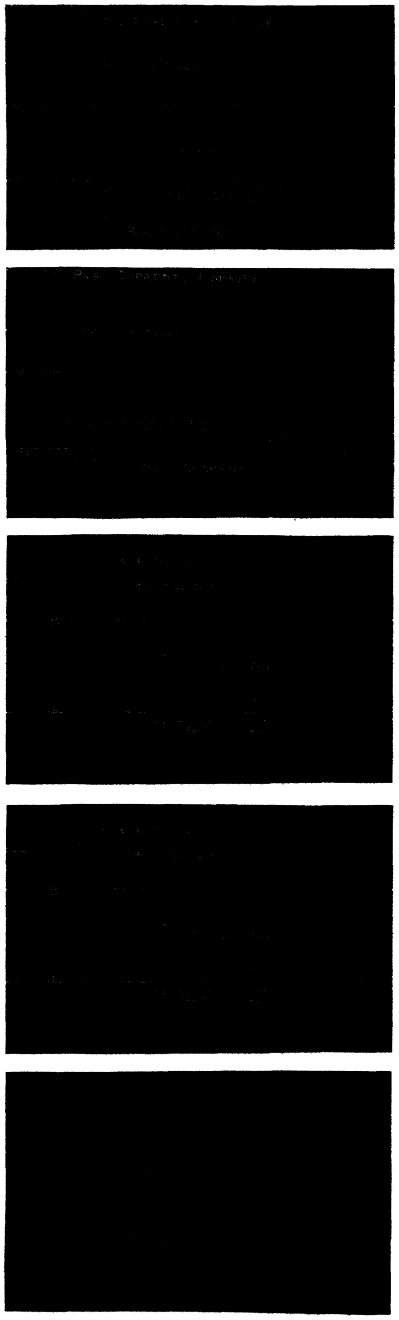


Fig. 8. Oscillograms of interruption and reversal after various periods of current flow in the low resistance direction.

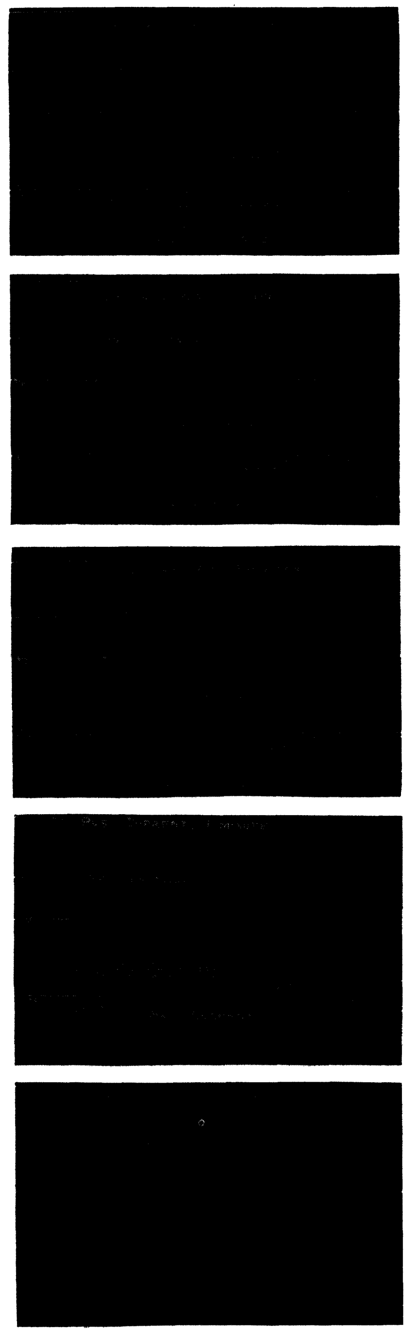


Fig. 9. Oscillograms of interrupuion and reversal after identical periods of current flow in low resistance direction to varying direction.

This characteristic need not be ascribed to a film. It *must* be ascribed to the building up of a resistance and a film appears to be the only source of such resistance. In Fig. 5 we show an oscillogram of current flow in the high resistance direction momentarily interrupted. In this case there is no condition of building up of resistance. The current flow returns immediately to its former value on reclosing of the circuit indicating that whatever is responsible for the high resistance persists in its existence throughout the interval.

In Fig. 6 we show an oscillogram of current flow in the high resistance direction interrupted and reversed. The current does not rise to its maximum value at once on the reversal. About 0.005 sec. is required. However, as shown in Fig. 7, exactly the same phenomenon is observed for the cupric

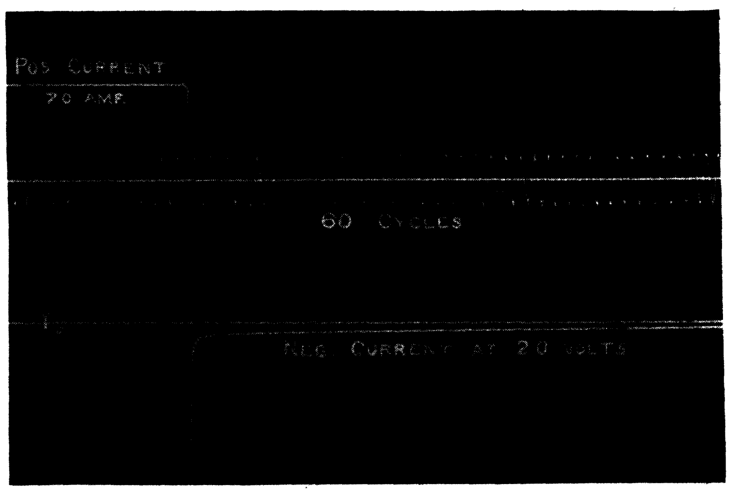


Fig. 10. Growth of resistance after reversal.

sulfide disk by itself between copper contacts. We would consequently be justified in saying that this oscillogram does not necessarily indicate destruction of the film lasting through that period of time. Indeed, the results obtained indicate that there is a gradual destruction of the film in a much longer time interval.

The method used in detecting this film destruction was: first, to form the junction by the regular method by applying an alternating current; second, to permit current to flow in the low resistance direction for varying periods of time; and third, to take an oscillogram at the moment of interruption and current reversal. In Fig. 8 is given a number of oscillograms taken after various periods of current flow in the low resistance direction. It is particularly notable as indicated by the increased time required to attain high resistance, that the apparent time of reformation of the film increases with the time that current has flown in the low resistance direction. Attention is pointed to the case of the unformed junction of Fig. 4 in which film formation was even slower. In this case the complete interpretation of the succeeding figure in the next paragraph should be in point.

In Fig. 9 oscillograms are given for current reversals from low resistance to high resistance after identical periods of current flow but with varying voltage in the high resistance direction. The lower the voltage the longer is the time required for the high resistance to develop. This is exactly what would be expected if a definite amount of work be required to form a highly resistant intermediate layer. The oscillograms at 0.25 and 0.50 volts are, however, more difficult to explain. In these cases we do not have reformation of the film at all.

One possible interpretation of this phenomenon is that on current flow for any long time in the low resistance direction and destruction of the film small, complete, low resistance contacts are made between the cupric sulfide and the magnesium and that these contacts behave like fuses and can be "burned out" only at sufficiently high voltages. Only after "burning out" has occurred does film formation ensue. Indeed, all we may be observing in the apparent reformation of film may be "burning out" of the contacts. In Fig. 10 there is an oscillogram of a similar current reversal in which the recording film was revolved at lower speed. It can be seen that although the resistant film develops almost immediately it continues to "grow" through approximately 0.25 sec. Fig. 11 is a typical oscillogram indicating the opera-

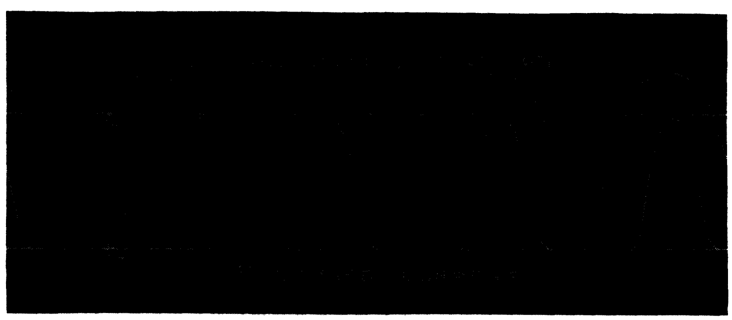


Fig. 11. Operation of a completely formed junction as a half-wave rectifier.

tion of a completely formed junction as a half-wave rectifier. In this illustration there is no sign of any destruction or reformation of a film in the time of a half-wave, but there is evidence that a certain critical voltage must be attained before current flow starts.

Battery and thermoelectric effects. The earliest explanations presented to explain contact rectification involved the propositions that rectification resulted because of a battery or thermoelectric effect within the junction. The first evidence contrary to this theory was presented by Braun,[4] the discoverer of contact rectification. However, this theory is repeatedly reinvoked for each new case of contact rectification and it is consequently necessary to examine the evidence in point that we have collected.

In Fig. 12 is illustrated in diagrammatic form the oscillograph circuit used for this study. *V* and *A* represent the voltage and amperage galvanometer vibrators in the oscillograph respectively. *J* represents the junction.

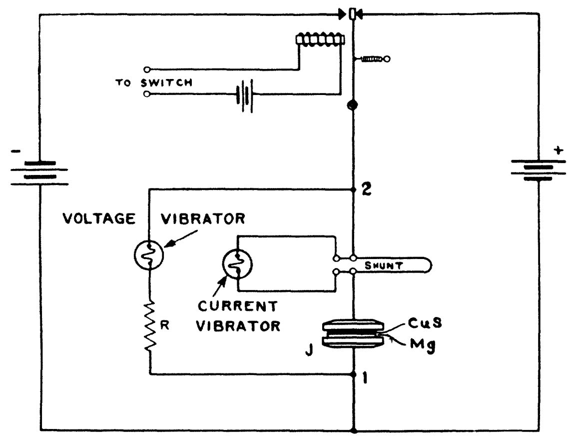


Fig. 12. Oscillograph circuit.

When current is flowing in the direction 1→2, the oscillograph can be adjusted so that the mirror displacements for *V* and *A* are in the same direction. If for any reason the circuit should be interrupted and there be a battery effect or thermoelectric effect opposed to the direction of the current, there should occur a reversal of the reading on *A* and a persistence of a deflection at *V* in the same direction as prior to the interruption. In other words, a reverse battery or thermoelectric effect will, on interruption of the

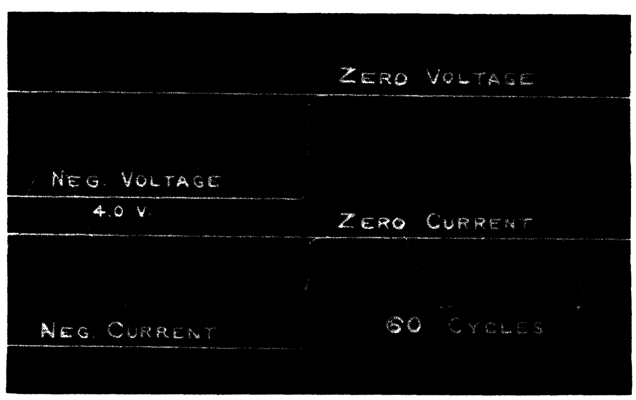


Fig. 13. Breaking circuit in high resistance direction.

circuit, give at least a momentary persistence of deflection of *V*. A failure to obtain this deflection, after interruption of the current in either direction, is indicated in Figs. 13 and 14. Particularly in the case of Fig. 13, where current flow in the high resistance direction is interrupted, would this persistence of the voltage deflection be expected. The purpose of the oscillogram at *A* is merely to give an accurate indication of the time of interruption of

Fig. 14. Breaking circuit in low resistance direction.

the circuit. It is altogether possible that there may be a battery or thermoelectric effect of insufficient intensity to give an opposed deflection at *A*.

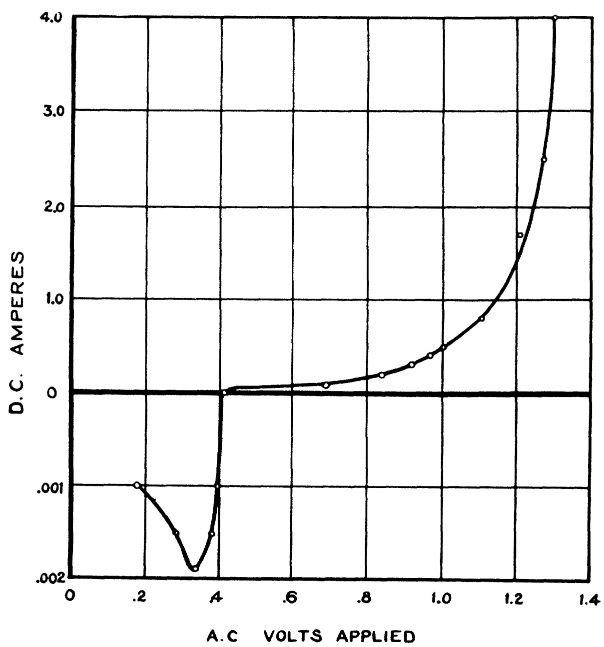


Fig. 15. Relation between d.c. amperes and impressed a.c. voltage.

The momentary opposed deflection on the current oscillograms of some figures at the moment of interruption is attributable to the inertial oscillation of the vibrator for it is similar in magnitude, direction, and period to the deflection on the voltmeter vibrator.

We may, therefore, conclude that there is no battery or thermoelectric effect in the cupric sulfide-magnesium junction of sufficient magnitude to account for its contact rectifying properties.

"Reverse rectification." The current efficiency of a rectifying junction has a theoretical maximum value for half-wave of 63.6 percent. It has been

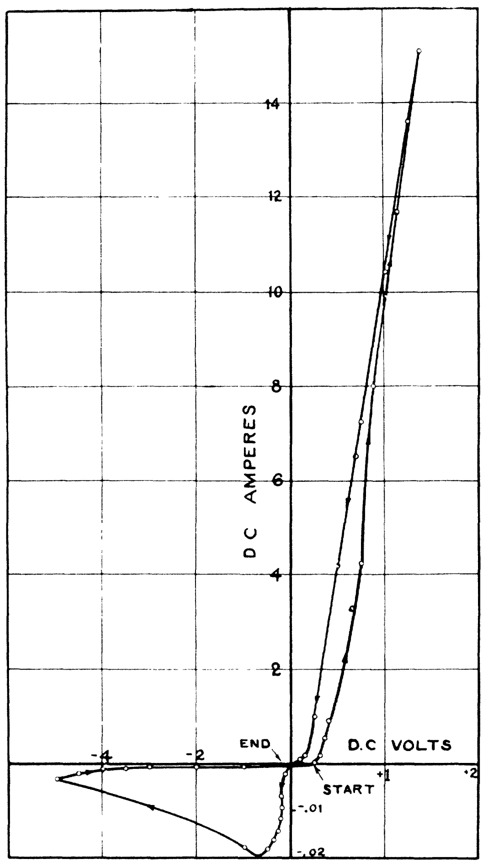


Fig. 16. Relation between d.c. amperes and impressed d.c. voltage.

known for some time that the current efficiency is a function of the applied a.c. voltage. For example, it is evident without any intimate knowledge of the properties of a rectifying junction that above some impressed voltage it will break down and cease to rectify. At that value it is obvious that the rectification efficiency is zero. It is not so well known that for some rectifiers the rectification efficiency decreases to zero at a small a.c. voltage. Goddard,[6] among others has pointed out that the direction of rectified current is sometimes opposed to the direction predicted by experience for the junction studied. For example, if for the cupric sulfide-magnesium junction the rectified current would flow in the direction magnesium to cupric sulfide, we would be observing the phenomenon of "reverse rectification." Tests that we have conducted indicate that the direction of rectification is related to the impressed voltage. The results are indicated in Fig. 15 in which we have illustrated a sharp reversal of current at approximately 0.4 volts a.c. A number of tests have indicated that the reversal always takes place in this region of voltage. It would be expected from this that the resistance of the junction would be lower at low negative voltages (i.e. from Mg to CuS) than at low positive voltages. This is verified by Fig. 16 in which the direction of taking current readings is indicated by arrows. In this figure also we may be impressed by the fact that there is an apparent destruction of a film which

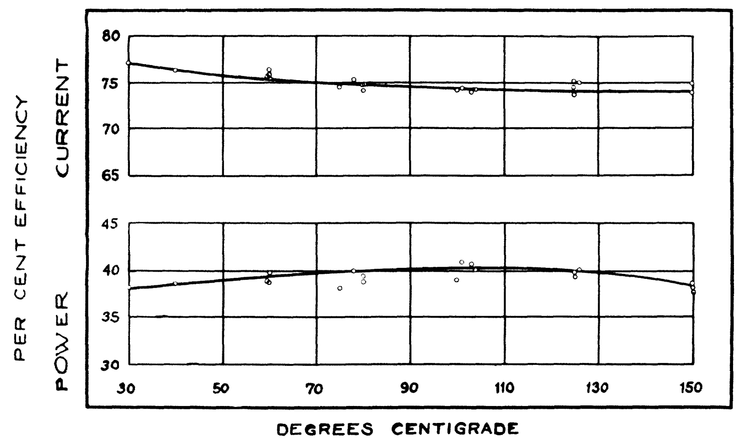


Fig. 17. Relation between efficiency of 4-junction bridge and temperature.

does not begin to reform until between -0.5 and -1.0 volts d.c. when reformation and negative increase of voltage are so rapid that no further readings are possible. This entire phenomenon is not made altogether clear in the light of the 0.25 and 0.50 volt oscillograms of Fig. 9 and the interpretation put on them. The conductive contacts, apparently, are of lower resistance than the film but we would expect them to carry current in both directions (if they do not "burn out") thus resulting in no rectification rather than in reverse rectification. The phenomenon will be subjected to further study.

Relationship between temperature and efficiency. The relationship between temperature and efficiency, for both power and current, is of great importance in the determination of the existence of a hypothetical film. Superficially, without too rigid analysis of the theories requiring the existence of a film in contact rectification, we may say that increase of temperature should be accompanied by lower current efficiency and, within limits, by higher power efficiency. A more detailed analysis of this aspect of the problem over a wide range of temperatures is reserved for a later paper. Fig. 17 indicates that this situation is true for a four junction bridge type rectifier.

The values graphed for power efficiency are arbitrary inasmuch as no correction has been applied for circuit conditions.

Conclusions

1. Oscillographic studies of the cupric sulfide-magnesium junction indicate film formation.
2. An explanation of the results obtained may be based on the hypothesis that "formation" of a film takes place on current flow in the high resistance direction and "destruction" on current flow in the low resistance direction for long intervals of times.
3. "Reverse rectification" is not easily explainable on any hypothesis so far presented. This problem is to be further studied.
4. The variation of efficiency of a bridge-type unit with temperature is in qualitative agreement with the requirements of theories that require film formation. This subject is to be discussed in greater detail in subsequent papers.
5. No battery or thermoelectric effect sufficient to account for the rectifying properties of the cupric sulfide-magnesium junction has been noted. It is consequently suggested that film formation and destruction are electrothermic rather than electrolytic in origin.

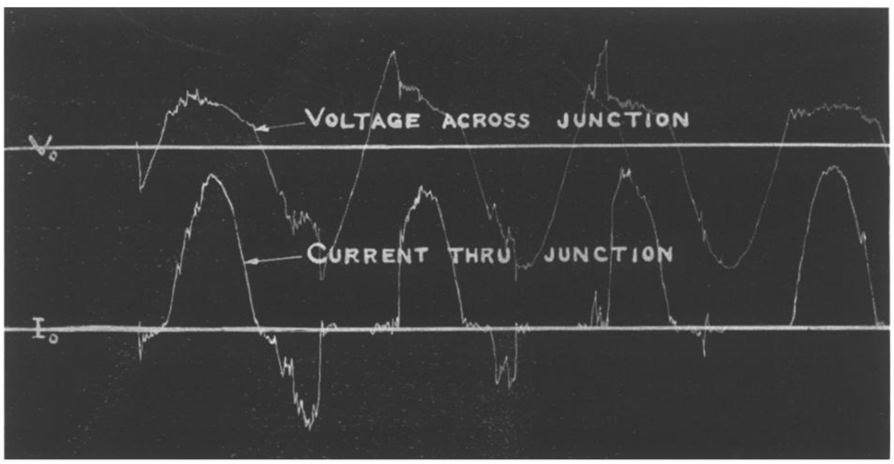


Fig. 1. Initiation of rectification.

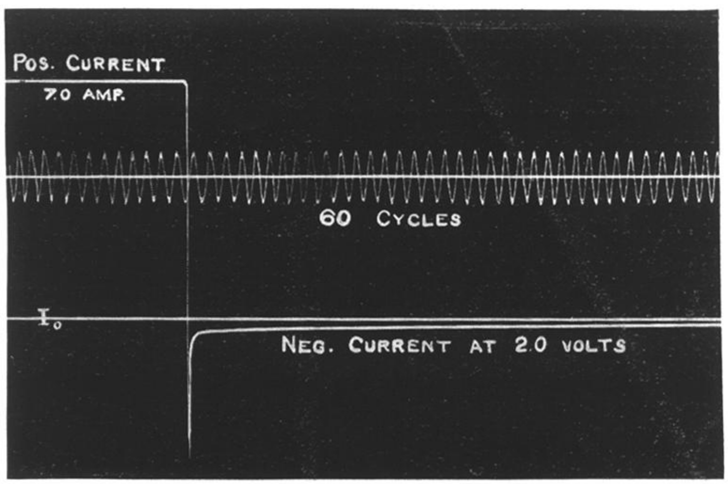


Fig. 10. Growth of resistance after reversal.

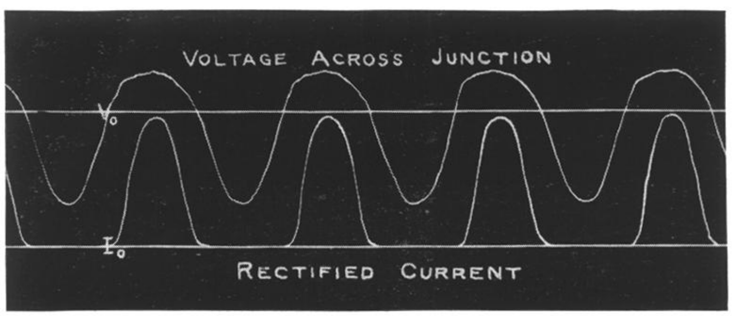


Fig. 11. Operation of a completely formed junction as a half-wave rectifier.

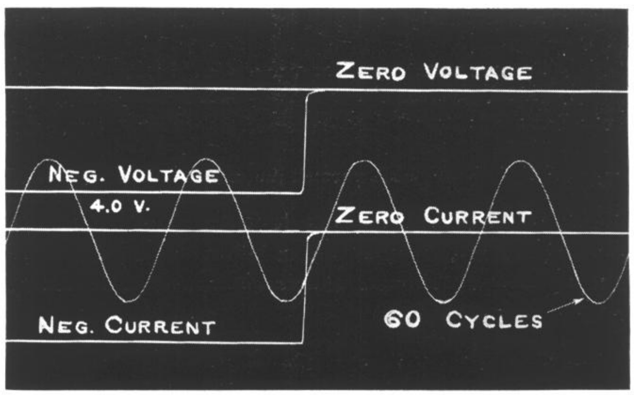


Fig. 13. Breaking circuit in high resistance direction.

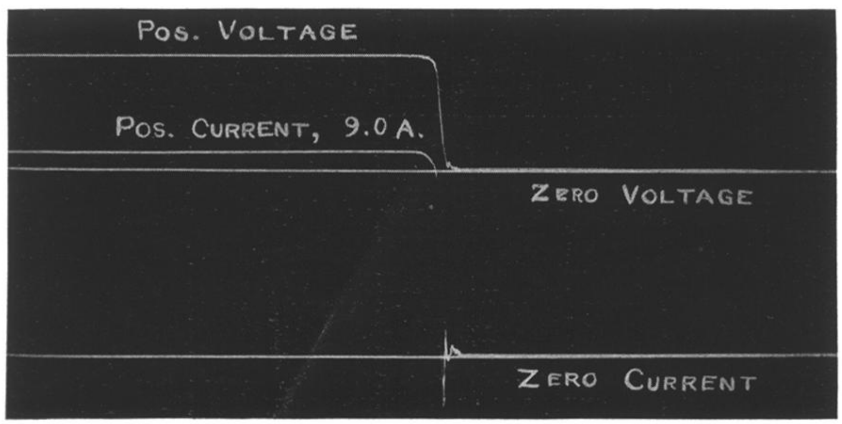
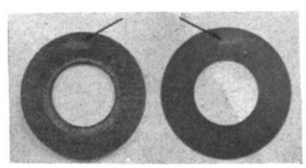


Fig. 14. Breaking circuit in low resistance direction.



CuS Mg

Fig. 2. Spots of adhesion.

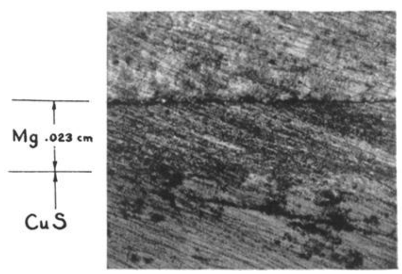


Fig. 3. Cross section of contact spot.

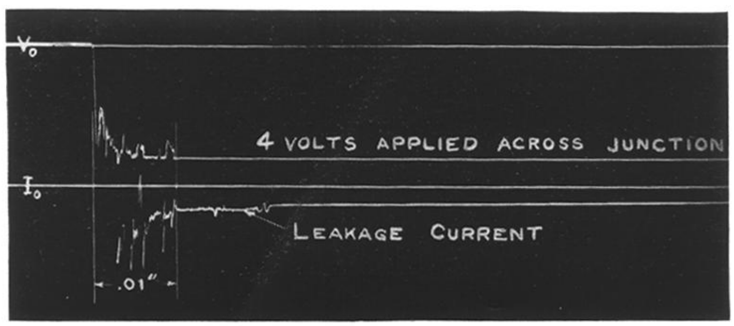


Fig. 4. d.c. formation of junction.

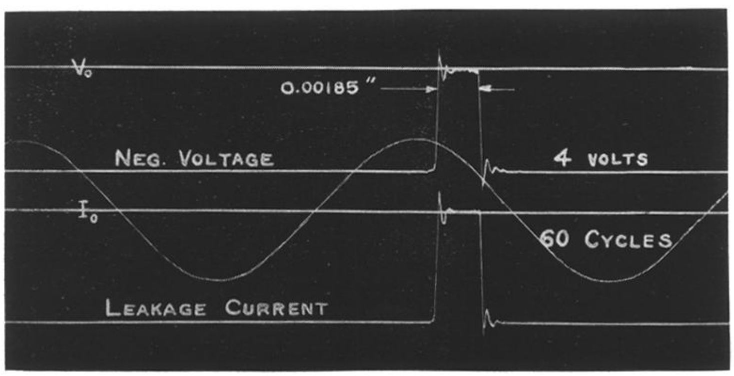


Fig. 5. Interruption in high resistance direction.

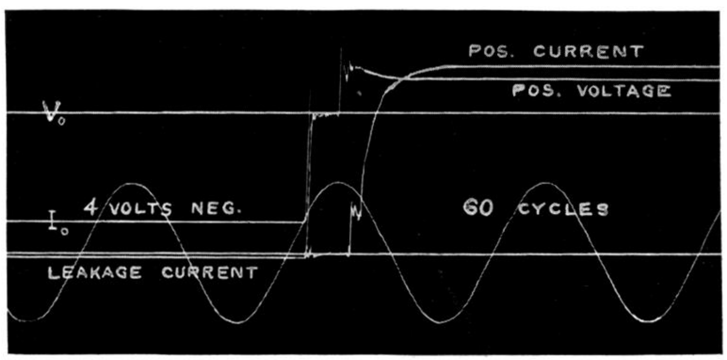


Fig. 6. Interruption in high resistance direction and reversal.

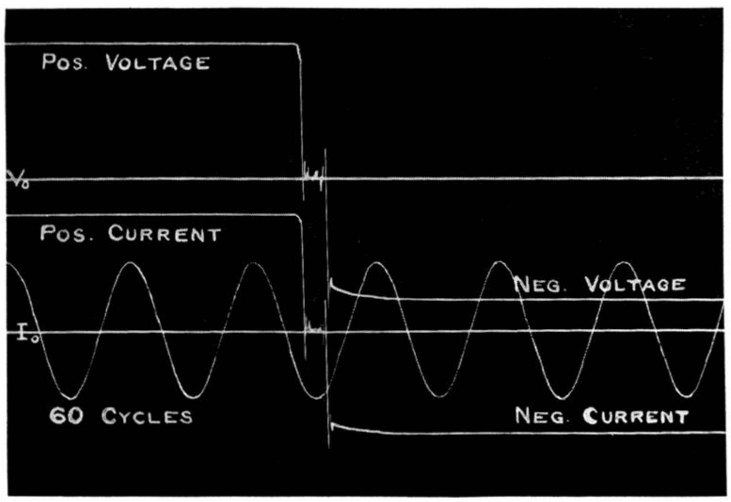


Fig. 7. Interruption in high resistance direction and reversal for cupric sulfide disk alone.

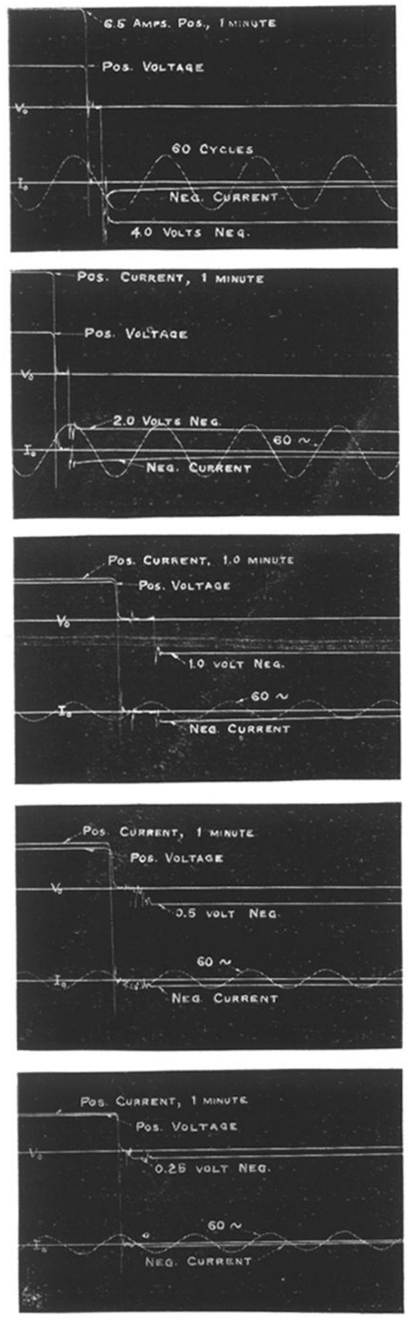


Fig. 8. Oscillograms of interruption and reversal after various periods of current flow in the low resistance direction.

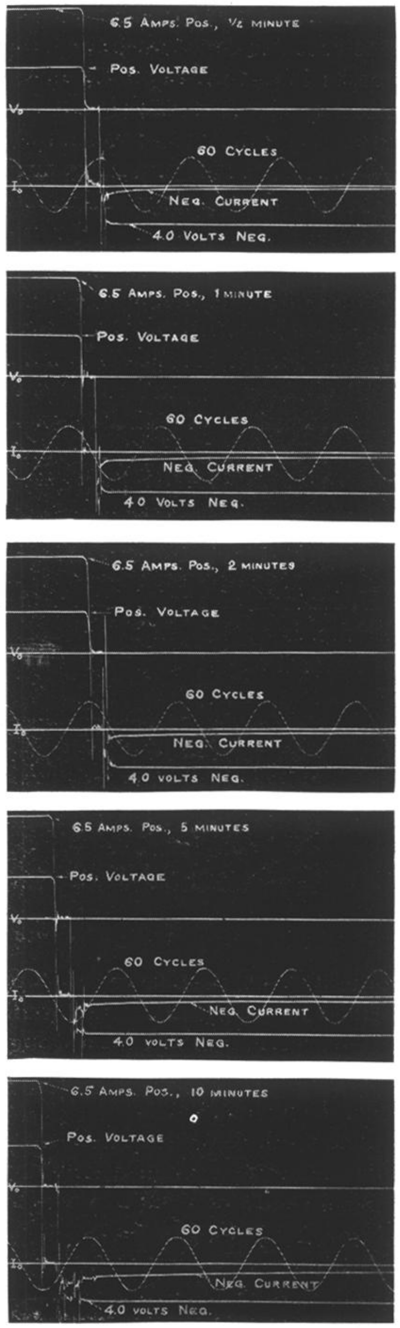


Fig. 9. Oscillograms of interrupuion and reversal after identical periods of current flow in low resistance direction to varying direction.