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CUPROUS OXIDE RECTIFICATION

A Thesis presented for
Professional Degree to
The Newark College of Engineering

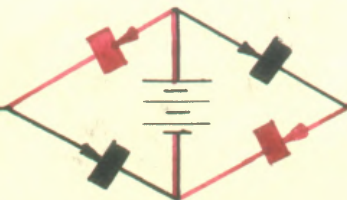
by

NEWARK COLLEGE
OF ENGINEERING

7592

Philip G.Cobb B.S.in E.E.1925

1928



CUPROUS OXIDE RECTIFICATION

PURPOSE:

It has been shown that cuprous oxide, when formed from a copper surface by suitable heat treatment, has remarkable rectifying properties towards alternating voltages applied through the oxide and copper. The purpose of our work was to investigate the effect fully from all angles possible, and especially from those considerations affecting the constancy and permanence in the electric circuit.

The work ranged from furnace operation to tests of completed units, and further to the development of a theory explaining as completely as possible this rectifying property.

It soon became apparent that here was ideal thesis material, and so, with proper permission, I have undertaken this rather complete report and now offer it as my thesis.

The work was carried on jointly by Mr. Rutger B. Colt, of Stevens Institute, Mr. Charles H. Bartlett of Brooklyn Polytechnic Institute, and myself.

In all a period of one year and three months was devoted to this investigation, and during that time we all were largely employed directly, although other matters claimed attention occasionally.

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The story of cuprous oxide in its natural form, cuprite, is shrouded in antiquity. It is definitely established that cuprite occurs in most deposits containing copper either native or in composition, and since copper was one of the first metals regularly and systematically used by the ancients it is entirely possible as well as more than remotely probable that cuprite was known as soon as copper. From a rather cursory investigation descriptions of this mineral have been discovered in fifteenth century works and one could probably trace it back much further. It is of a beautiful crimson tint when polished and for that reason attracted the attention of the philosophers as well as the more utilitarian of the scientists who were interested because of the high copper content. Cuprite is easily reduced by charcoal at high temperatures and so represented one of the sources of that *aes cuprum* mined in the days when Crete was building her civilization and power; a civilization that later transplanted gave the world that galaxy of minds, Plato the philosopher, Archimedes and Pythagoras the scientists, Hippocrates the physician, Homer the poet, and all those others whose conclusions were to be venerated for a thousand

CUPROUS OXIDE RECTIFICATION

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years more in still other continents, other religions, and other peoples.

But to return; history is after all an introversion which leads only to confusion. From the geologist's viewpoint the most complete description of cuprite is found in Dana's Minerology, Van Nostrand 1892, in which we find:

CUPRITE Cu_2O .

Aes caldarium rubro fuscum - known previous to 1758 and described variously as Kupferglas, Plush Copper Ore, Red Glassy Copper Ore, Mine Rouge de Cuivre. Isometric with trapezohedral hemihedriam, in octahedrons also cubes and dodecahedrons sometimes cubes lengthened into capillary forms. Brittle; Hardness 3.5 - 4 and Specific Gravity 5.65 - 6.15 Refractive Index high 2.849 (Fizeau) Occurs in Thuringia, Tuscany, Elba, Crete, Cornwall, Lyons, Ural Mountains, South Australia, Chile, and in the United States at Somerville and Flemington New Jersey. Also artificially as a furnace product and as a recent formation on buried copper coins and bronze utensils (Fletcher Min.Mag.May 7, 1887)

And now we shall turn to the metal itself. Copper has inevitably the same history as cuprite but for our discussion we are interested mainly with its melting point, 1083 C.

CUPROUS OXIDE RECTIFICATION

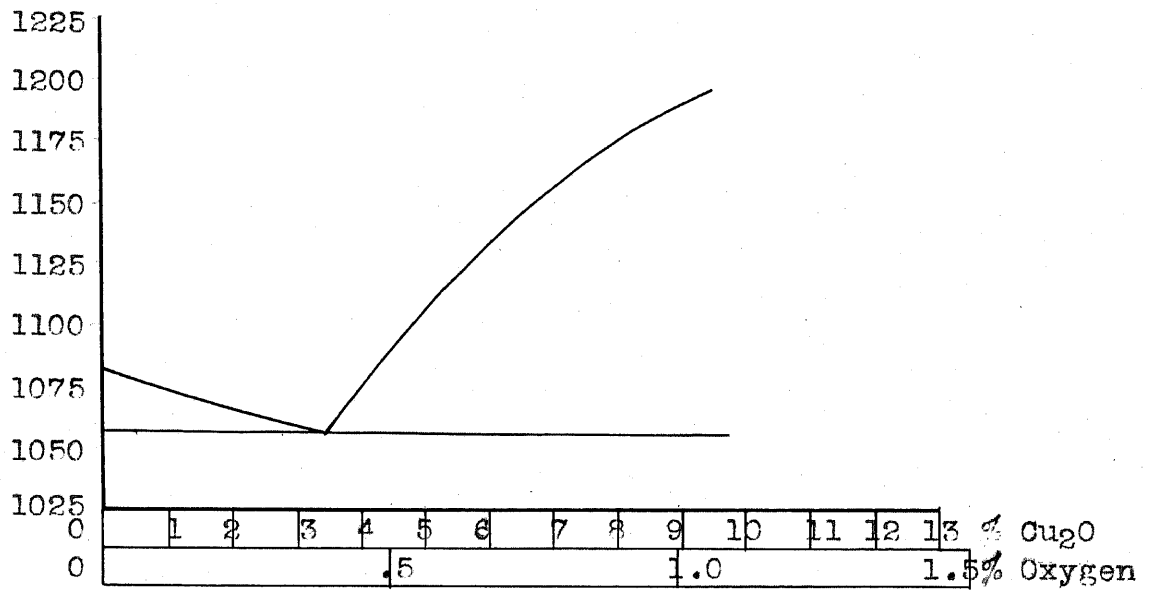
HISTORICAL

Many figures in and around this value are given and it is probable that they differ only in definition, that is degree of melting. For copper has no clean cut melting point but it becomes plastic over a considerable range of temperatures before it is transformed completely. We have observed a distinctly plastic condition at 1050 C.

Copper has the property of alloying with, or dissolving cuprous oxide when in a molten state, so we are informed, and this has been confirmed by us in our work. Gulliver's Metallic Alloys (Charles Griffin, London 1921) gives us an equilibrium diagram showing an eutectic at 3.5% Cu_2O , where the melting point is 1066 C, the composition being chemically 0.39% O and 99.61% Cu. From this point up or down the composition scale the temperatures of melting rise, to the melting point of copper at 1083 C and to that of cuprous oxide at 1174 C. This diagram was made by Heyn and first appeared in Zeitschrift fur Anorganische Chemie 1904 Vol XXXIX p 1. It is reproduced herewith.

Microscopic examination of prepared alloys shows that the oxide exists as a finely divided mass of blue globes on the yellow background of copper and this without any etching.

With this review of the materials themselves we must include another phase, necessary for our discussion. To introduce electricity one must again seek out the Greeks and trace an investigation from a fluff of wool clinging to an amber distaff through the discovery of the magnetic



Degrees Centigrade.

EQUILIBRIUM DIAGRAM FOR COPPER-CUPROUS OXIDE ALLOYS.

As given in Gulliver's Metallic Alloys ,
 Charles Griffin and Company, London, 1921.

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compass, through the work of Volta, Franklin, Henry, Faraday, Maxwell, Fleming, de Forest, Steinmetz to our great and ramified electrical science of today. And further to a small portion of the knowledge gleaned in the last quarter of the last century when coherers were used for detecting radio signals. And that is the fact that cuprous oxide, either natural or artificial, with or without contact with copper could be made to serve as a rectifier for alternating currents.

As a byproduct of the radio industry before the introduction of the a.c. tubes there were devised many types of rectifiers for use in charging the wet batteries then used to supply power for the operation of the home receiving sets, and in the Scientific American for May 1926 there appeared an article describing a new and promising type made by use of cuprous oxide disks arranged in a bridge circuit for full wave rectification. It was this article which prompted the authorization of a complete investigation of this material and which gave this work its being. Although our work was never reproduced commercially two types did appear, one by the Westinghouse Company and one by the Kodak Company. Neither type was ideal although both operated fairly well, with the greater success resting with the Westinghouse type developed by Ghron Dahl, and described in part in the A.I.E.E. Journal for March, 1927.

The basis for our work, therefore, lay in the knowledge that the oxide deposited on the surface would rectify, and from this we planned our course. Our first step was to discover the means that could be used in depositing the oxide. We found that there were two, both a matter of heat treatment. The first, and the one that had been used for years previously utilized saltpeter heated to 900 degrees Fahrenheit or above. The copper is dipped into the liquid saltpeter to remain for some time before it is withdrawn and quenched in water. When examined the copper has a black coating of the cupric oxide and beneath the red of the cuprous. Cupric oxide is stable at lower temperatures than cuprous and so when the piece is removed from the bath into the air the outer surface changes by the absorption of oxygen to form an adherent coat which prevents any further change. When this outer coat is removed the red oxide is exposed. As has been said, this material possesses a natural beauty of high order and consequently has been sought after for a fine finish on cases for scientific instruments, lamps and other decorative pieces and generally for metal furnishings where durability, long life and resistance to atmospheric reactions made it desirable. The older type of Weston Portable Standard (Model I) was finished in such a manner as one example.

Since we had had some experience with this method in previous years we tried the saltpeter bath first, testing the current passed or forward current and the leakage or back current with direct voltage in circuits of constant resistance and voltage on specimens of the same area. We were partially

successful in that ratios as high as fifty milliamperes forward to one reverse were prepared, but the resistance was high in both directions and it finally became evident that we had to search further for another method.

Contemporaneous with our salt bath work we had pursued another line of investigation, briefly but with some promise of success. From other metallurgical work we knew that cuprous oxide could be formed directly by the exposure of hot copper to the oxygen of the atmosphere. This fact is well known and the action is described in all texts covering copper and its metallurgical reactions. Heretofore interest had centered around the removal or prevention of the oxide as it increases the resistance as well as produces a more brittle "cold short" bar.

Our problem was the reverse. We were deliberately to seek the oxide. Our first work was done crudely enough in an available gas furnace. First we used long thin strips of copper scrap in the hopes of showing some signs of the oxide. Our method lay in heating the strip to as close the melting point as possible without actual liquifaction, and then plunging the strip into water. Many were lost by melting, all came out covered by the cupric oxide but in every one there existed unmistakable evidences of the cuprous oxide coating that we sought. The furnace used was a round crucible type with four burners at the base at an angle so that the mixed gas and air would swirl and combine as they travelled upward.

This action was not complete, nor was the oxygen content constant from the bottom to the top of the furnace. We noted on many of our strips that the cuprous oxide while still in the furnace and hot, could be reduced back to copper by exposure to the reducing flame in the furnace. And this was one of our most important discoveries. For what could be more ideal than a layer of copper as a contact surface on one side and the parent copper on the other. But it had come too soon for immediate exploitation. We decided to let the contact problem rest until we had arrived at a more perfect form of oxide. I shall refer to this decision in another and later discussion. Suffice to say that it took a long period to correct the false logic of our minds on this point. We next decided on a temporary design for our unit rectifiers and selected a sort of washer shaped piece that permitted of ready mounting by bolts passed through the center into a bridge circuit connection for use in testing.

Still using the gas furnace we rigged up an iron strap for supporting a single disk and we proceeded to oxidize a number of disks at rather random conditions of furnace temperatures and atmospheres, partially through design and partially through lack of suitable control. We discovered that with skill one could produce a substantial thick coat of oxide and we went so far as to quench the disks within the furnace and thereby secured disks with no cupric oxide on the surface.

This was done by lowering a small pot of water into the furnace just before we desired to quench the copper. As was said we found it impossible to secure any uniformity by this method. But the fact we wanted had been established. One could produce a smooth, clean, adherent coat of cuprous oxide on a copper surface by heat-treatment alone.

Next, of course, we became interested in refining our process; refining is perhaps too close a term, rather discovering what our process was. The temperature was of course the main point, and we needed as well the time and the oxygen conditions. There were two optical pyrometers available, a kerosene "Bunsen" Pyrometer and an electric pyrometer operating on somewhat the same principle. In both the color of a calibrated lamp is compared with that of the heated piece and the temperature discovered by reference to calibration data furnished with the outfit. Time was, of course, easy enough to read, while the oxygen content of the furnace gasses was observed by means of the appearance of the copper. To a practiced eye it is easy to see the change from the pale green denoting pure copper to the yellow of the oxide as the disk is held in various parts of the furnace, this change taking place only when the copper is at or near its plastic point. This color phenomena introduced a difficulty into reading the temperature by optical means since the radiation is affected materially by the change in color of the material.

Nevertheless we found that we were working just under the melting point of copper for the best appearing oxide, and that we could drop the temperature considerably and still secure a good coating of the oxide. Further that the longer we kept the disk in the furnace the deeper the penetration. And lastly that we could come to no definite conclusion as to the best atmospheric condition for the highest ratio. Our ratios were still about fifty milliamperes forward to one in the reverse direction on a two volt battery directly connected.

So we decided that our process needed further refinement. This decision, I may add, occurred often in our subsequent work. We felt that gas was not the ideal fuel, at least when burnt without muffle protection for the disks, and so took a small electric furnace (similar to a dental furnace) for our next step. This was a resistance type and of course was susceptible of accurate control by external resistors. We secured in addition a platinum-rhodium couple which was installed through the cover to approximately the position of the disk. Calibration was made by observing the time-temperature curve of copper during its solidification period. A clearly defined "arrest" was observed which gave us the temperature in millivolts of the melting point of copper.

We planned to work just under this point and did, but found in addition that there was also a plastic range under the true melting point in which range the copper acted like

slush ice; some was liquid, some solid, the whole could be stirred and manipulated. Lower yet there was a range in which the copper lost most of its mechanical strength. While retaining its form generally we found the disk drooping and deforming in the furnace. It was just under this deformation point that we worked. Again we tried to evaluate the effect of oxygen supply on our disks with no definite conclusions. Our ratios had come up to about one hundred to one but the results were exceedingly variable as far as our ability to reproduce the units was concerned. Good and bad were produced by the same method and often consecutively.

We now returned to that earlier discovery of redepositing copper on the surface and soon found that in addition to securing the results by atmosphere in the furnace we could produce the same effect by selecting a suitable quench; one that had reducing properties. There are many of these. We have used with varying success cylinder oil, kerosene, gasoline, alcohol, varnish, linseed oil, glycerine, sugar solutions, ammonia and other reducers.

So our process then stood as oxidation within the furnace until a heavy enough oxide was formed and then an immediate quench in a solution which would reduce the surface oxide as well as cool the disk. Our output per disk increased greatly; but our ratio of forward and reverse currents did not change. We had reduced the contact resistance only and had not materially changed that other important characteristic, efficiency.

The efficiency was measured in a conventional manner but gave a true comparative indication of disk to disk variation. I may add that we measured the a.c. watts input and the d.c. current and battery voltage for output. This leads to an anomalous condition since the output rectified current is not directly an Ohm's Law value, but is considerably less due to the voltage of the battery. Since our rectifiers were intended for battery charging however, we consider this efficiency as satisfactory, taken as it was under the higher voltage and lower current values for which the units were to be used commercially.

As an experiment we now rebuilt a gas furnace of the open type so that we could use it on quantity production, our endeavor being to evolve a successful feeding and recovery system by which some of the variables could be eliminated. In its workable form this oxydation system consisted of an inclined channel mounted on rollers and held in the low position by springs. At the lower end we mounted a cam and shaft so designed as to give the channel a slow upward motion and a gentle release depending on the springs to bring the channel against the stops and this impelling the disks further on the slide by inertia. By varying the speed of the cam and the angle of the channel we were able to control the time taken for each disk in traversing the length of the furnace. A chute was arranged at the lower end which would by gravity convey the hot disks to the quenching tanks below. As was said this machine was built to determine the possibility of semi-automatic production. It proved successful from the point of view of

production, and reproduced well the laboratory method as we knew it. But we still had a long way to go before we could call the process perfect. The efficiency had not been affected by our reduction of the top surface to copper, although, as has been said, the output was increased.

It was during this period that we first considered the rate of penetration of the oxygen into the copper. It seems quite logical to assume that a layer of atomic thickness is oxydized first and that this oxygen that exists in the combined form is relayed to the next layer while more atmospheric oxygen is being absorbed by the first and so on for as long as the disk is subjected to the high temperature. That is the only way to account for the presence and penetration of oxide to any appreciable depth, and we have created adherent coats as thick as one-sixteenth of an inch by extended treatment. We felt in this connection that the oxygen would penetrate quickest at first and then at a reduced rate after an appreciable layer had been formed. Our first efforts were directed toward the control of the furnace atmosphere, cutting off as much oxygen as possible at the start and the increasing the supply later so that a uniform rate might be secured. This did not seem to affect the results in any conclusive fashion so we decided to go still further for confirmation.

We planned to coat the disk with a combustable material which would burn off and absorb most of the oxygen at first, then allow the oxygen freer access later. We

discovered a rather remarkable thing. The greases, varnishes and pitches used burnt off much too quickly to have affected the oxygen penetration during the five minutes of heating, but our results were surprisingly good. Here for the first time we found that it was possible to decrease the forward resistance materially without getting a proportional decrease in the back resistance. Just what the action of our various coatings was is still unknown, but we had established vicariously the fact that it was impossible in consider our ratios as fixed.

It was at this point that a metallurgical microscope became available, and we first saw what we had been producing. Th microscope was a Leitz standard machine with bellows attachment for photographs and eyepieces for visual examination. With the machine and combinations of eye-pieces and objectives it was possible to examine specimens at magnifications from 25 to 2000 diameters fairly readily. Our first work was done at 150 diameters, and later we went as high as 500 for our regular examination. Attached to this report there is a typical photomicrograph of the type we used in our determinations. As can be seen we had a cellular structure under consideration and many marked characteristics were recognized. Our method of examination lay in etching the top surface with cyanide or ammonia and then examining the resultant structure, after which we chipped off the oxide coat and examined the copper surface exposed. It was this surface which gave us the most information. It is seen that the copper surface has a primary cellular

marking and by close examination there can be discovered a secondary marking entirely independent of the primary. In addition we find pit holes or dark specks as they appear in the photo. On other specimens, unfortunately not photographed there can be seen well marked "slip bands" in addition. A "slip band" to a metallurgist is what a fault is to a geologist. Stead in his work gives us some excellent views of slip bands in steel, as does Osmond. This may be compared to the tilted geographical faults in which different strata become up-ended and appear layer for layer at the earth's surface, generally during a chaotic state. The pressure being too great, the rock structure is tilted out of its normal plane during the relief. So with the metallurgical slip band. Only a pressure condition can produce the effect, and so we concluded that there was considerable transverse pressure between the copper and oxide during the formation period or during the quenching. Our assumption of pressure was further substantiated by the fact that during quenching the oxide on the edges of the disk would fly off at a really high velocity due to the shrinkage at unequal rate between the two materials. A piece of oxide so small that it is not readily discernable to the eye would snap off the disk, travel a foot or so in the air and still strike with enough force to make its presence felt appreciably. Fortunately few large pieces dislodged themselves.

From a series of runs made for the purpose of microscopic examination we found that the best structure for

for forward current was a large primary mottle with the dividing lines clear cut and for the lowest back current a surface with the fewest pits; it was impossible to link the secondary mottle with any factor. We found that the factor exercising the greatest influence was the temperature at which the disks were oxydized. The nearer the plastic the better the disk for output and efficiency.

Our summary of the work so far is given herewith:

March 3, 1927

A. Cuprous oxide forms directly in air above red heat.

Cuprous oxide-copper eutectic forms at or above 1064 degrees centigrade.

In an excess of air at red heat some cupric oxide is formed.

Cuprous oxide forms more readily at higher temperatures.

Cuprous oxide will be reduced to copper at higher temperatures in the presence of any reducing gas such as illuminating gas.

Cuprous oxide melts at 1160 degrees centigrade.

The quench cools the material quick enough to prevent the formation of cupric oxide, and when a reducing quench is used copper is redeposited on the surface.

B. Under certain conditions simple tetragonal crystals are formed whose principle axes seem to be normal

to the copper.

Cuprous oxide also forms octahedral and dodecahedral crystals as well as intermediate forms.

When the crystals are treated with cyanide they are reduced leaving a skeleton of their former shape.

In etching the metal is usually attacked more readily at the inter-granular boundaries.

Impurities are usually found at the crystal surface.

Of our method as developed so far we had reached the following conclusions:

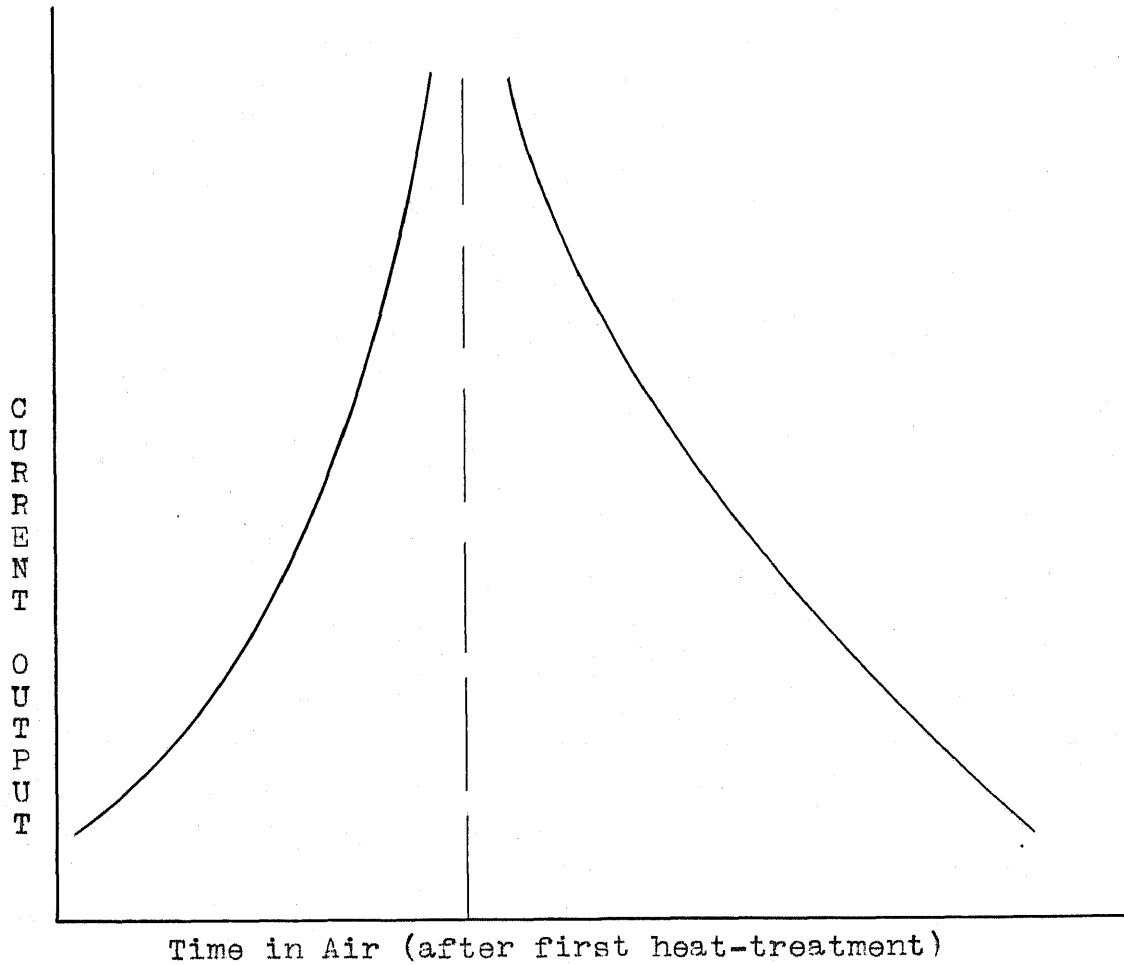
The stability of operation leaves much to be desired. It is sufficiently stable for production however, and the disks produced will make fair rectifiers.

Time seems to have little effect on quality but does have an effect on the breakdown of disks exposed for a short time to the furnace temperature. This is due to the thinness of the coating given.

Temperature controls the penetration to a great degree, and the higher the temperature the greater the penetration.

The rate of penetration does not seem to affect the quality of the product, although greases and varnishes used as coatings produce better disks.

And so we leave this phase of the work to enter the discussion of another discovery of a remarkable nature and of far-reaching effects.

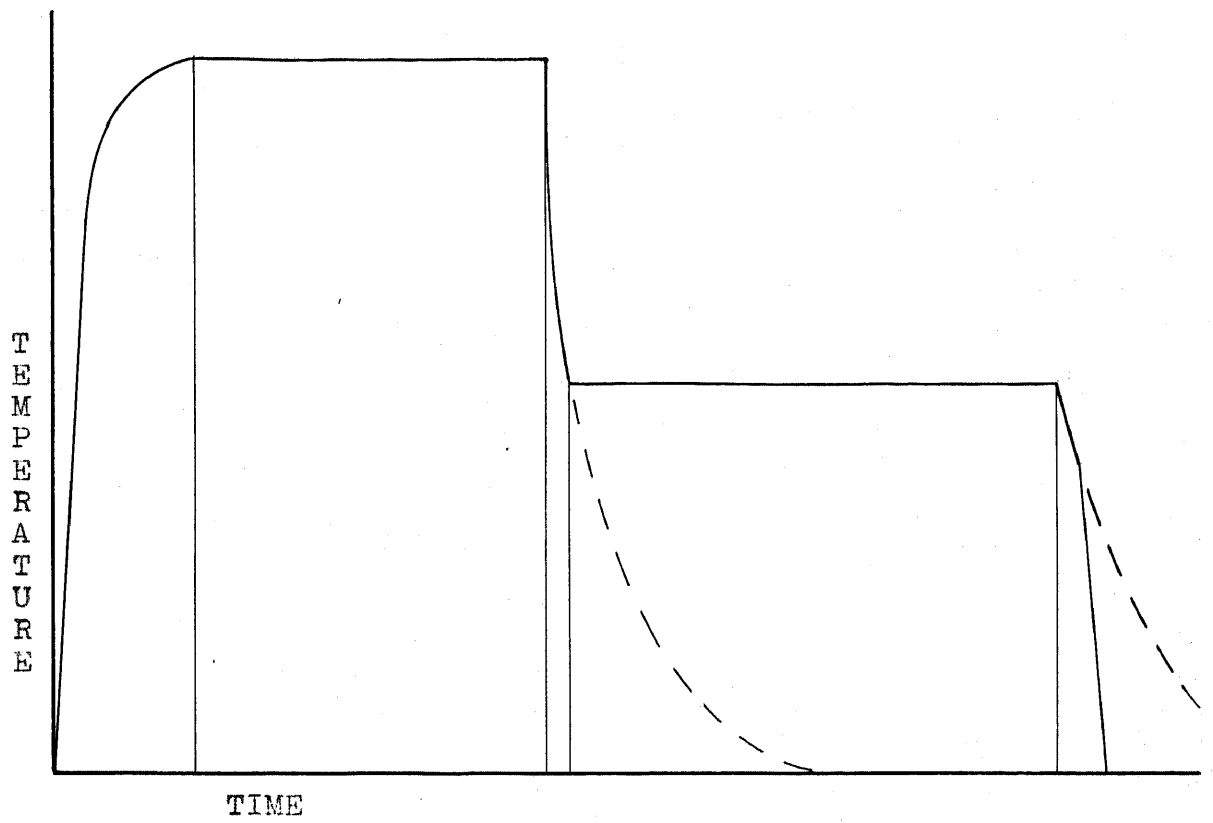


A curve illustrating the variation of output current with the time in air after the first heating.

The fact discovered is given best by the accompanying curve illustrating the variation of output current with the time in air after heating. It can be seen that by exposing the disk to the air for various times before quenching that the output is increased along a regular curve to an indeterminate point, after which, the reverse becomes true. So for constant furnace temperature we had found a way to vary output by exposing to the air. This time in air means additional oxygen supplied and a drop in temperature before the quench and we found that it was the drop in temperature which had the greatest effect. This method was checked and cross checked by various methods and at various times with very consistent results.

We now set out to determine the effect of furnace temperature and of time in furnace on the curve. The temperature was found to alter the entire curve up or down as the furnace was heated higher or lower, in addition to altering the maximum point slightly toward a longer time in air for the higher temperature. The time in the furnace affected the thickness of the oxide and so was eliminated as a factor of experimental importance. The only necessity for considering time was that of getting an oxide thick enough to provide electrical strength against breakdown and this was easy to do.

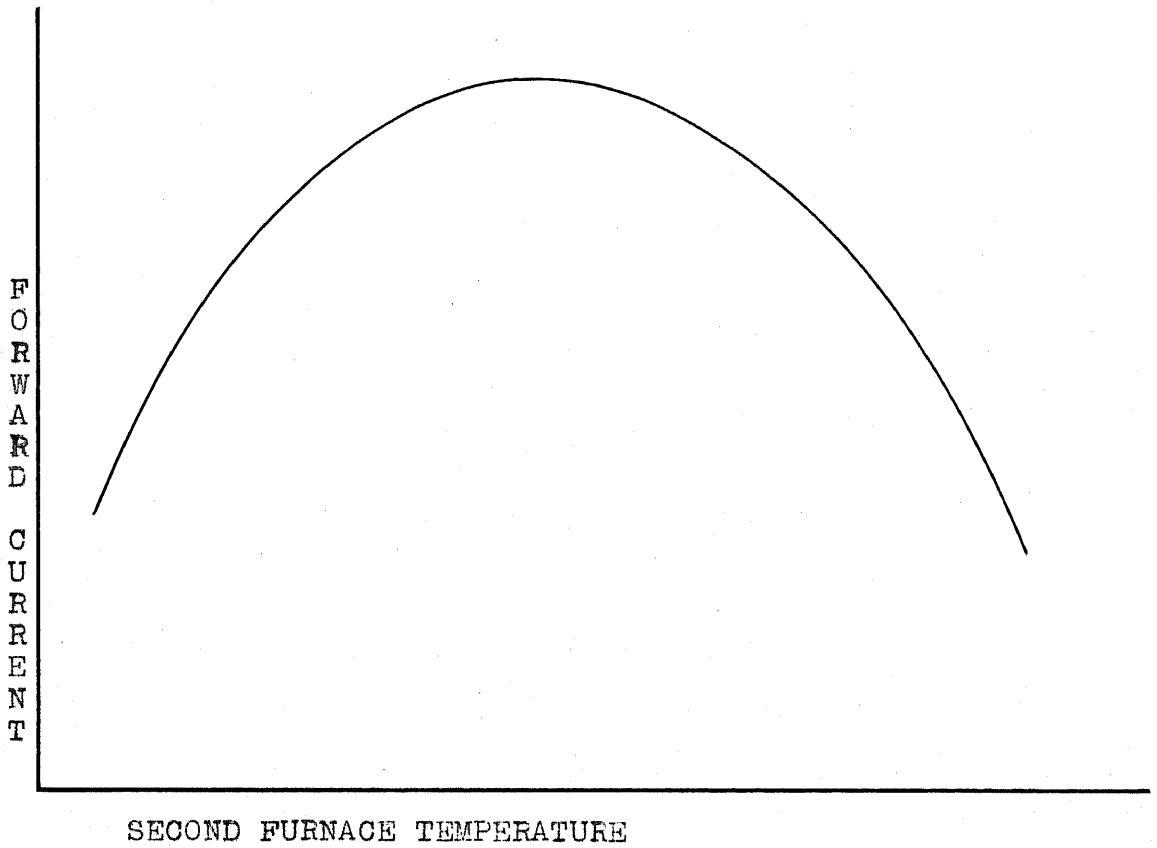
To come back to our first point and summarize, we found that there was an exact temperature lower than that of the furnace temperature which would produce the best rectifiers.



A Temperature-Time cycle for producing disks.

After this conclusion, it was easy to vision a second furnace at this exact temperature so that we could eliminate the variable factor of air cooling. At the same time, we began to vision a time temperature cycle for producing the rectifiers, as shown on the curve so designated.

From the curve it can be seen that there is first the rise to the temperature of the furnace. This can be controlled to an extent by varying the mass of material to be heated. I may add, that we never found any great variation due to this cause, which, we investigated by stacking various numbers of disks together and testing the top one alone. Next on the curve comes the line of constant temperature in the furnace. This is of interest only through the necessity of securing coating thick enough for protection against breakdown. Next comes the drop from the first to the second temperature. Here is a problem indeed, since it is possible to alter the cooling curve so that a greater or lesser time than that required in air would be consumed. This introduced considerable experimental work. To secure a very sudden cooling to the second temperature we arranged a salt bath similar to the baths used in hardening steel. We adopted saltpeter since its effect other than that of cooling would be beneficial. The disks were quickly removed from the first furnace and plunged immediately into the bath to remain for various times. Then for the other extreme we used a second electric furnace and passed the disk from one to the other as quickly as possible. For the intermediate, of course, we used an air cool to the second temperature and then inserted the disk in the second furnace. Results varied somewhat, but with no uniformity such as marked the air cooled curve. It is



Curve illustrating the effect of the temperature in the second furnace on the forward current.

hard to emphasize the value of this first air cooled curve. It gave us, of course, a greatly increased output for one thing but it gave us, too, an indication of the certainty with which results could be duplicated with the material so that in our later work we could be sure that inconclusive results meant that there was no major effect which our experimental work was missing. And here we decided that there was no great gain by any of the methods of dropping from one temperature to the other, and no great loss either. Later we found that either the air cool and insertion or the immediate insertion gave excellent results. The bath method was dropped for another result. We found it impossible to redeposit an adherent coat of copper over the oxide by this means.

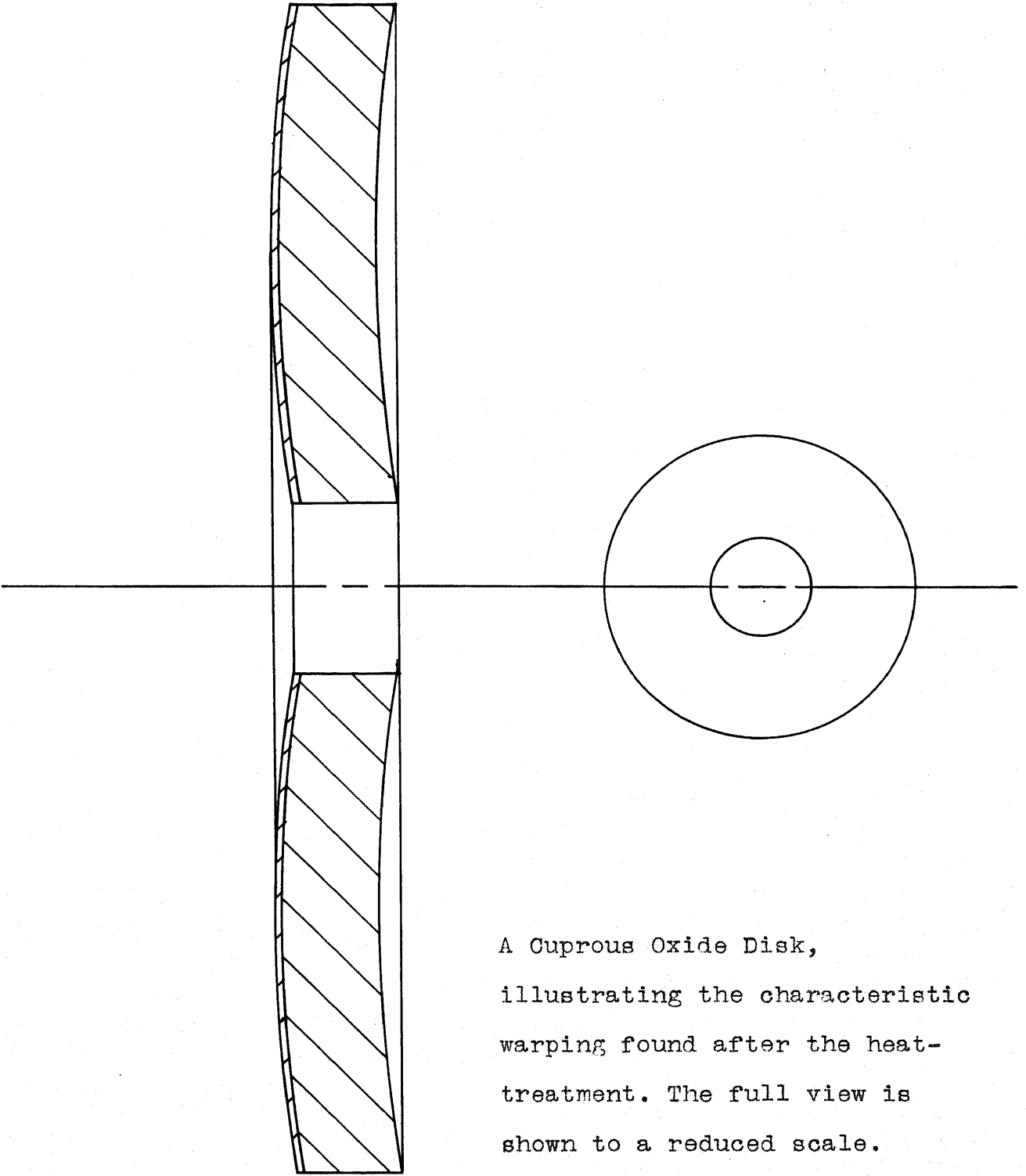
Next on the curve we come to the line of constant second temperature. This can be varied but we found it important to a limited extent only. It is certain that up to a certain point or time this treatment is necessary as a ageing or settling treatment and after that there is no appreciable gain or loss. It is possible to vary the second temperature up or down and the effect is noted on the curve titled "Curve illustrating the effect of the temperature in the second furnace on the forward current". Here again we find a regular variation with a rather well defined maximum but instead of approaching the maximum critically as in the air cooled curve, this curve approaches and recedes at a lower rate. This allows us some appreciable variation in the second temperature without great loss in output. This factor is of prime consideration when a commercial process is desired.

To revert to our time temperature cycle again we have reached the point of quench from the second temperature to room temperature. This quench embodies two things. First, reduction in temperature and second a redepositing of copper on the surface by means of some liquid reducer in the quenching bath.

Many experiments were made over this point as to speed of quench composition of the bath for best copper and best output composition for the most stable quench, and for the temperature of the quench. And we found them inextricably connected so that no real decision could be made as to the one best plan. For example, a quick "plunging" quench requires a stronger reducer than a slower "dipping" quench and, therefore, a different composition. At the same time the temperature of the quench affected the plating of the copper greatly, giving a stronger coat for higher temperatures. As our reducing quenches are all volatile we must keep the temperature down as much as possible to avoid loss of the reducer. In addition some of the reducer is always used when copper is dipped into it so we never could achieve an ideally stable solution. Our only solution was then empirical.

There is no best, but there are many satisfactory solutions. Space and other considerations prevent a further detailed account of our work on this point but it suffices to say that when we completed our work we had three general schemes calling for different compositions of quenches which gave good results. One gave us the highest forward currents with a slightly high back,

the other gave us low forwards and backs, the last gave us an intermediate condition. I can add in reiteration that our units were tested individually and then collectively in bridge connection for efficiency and output.



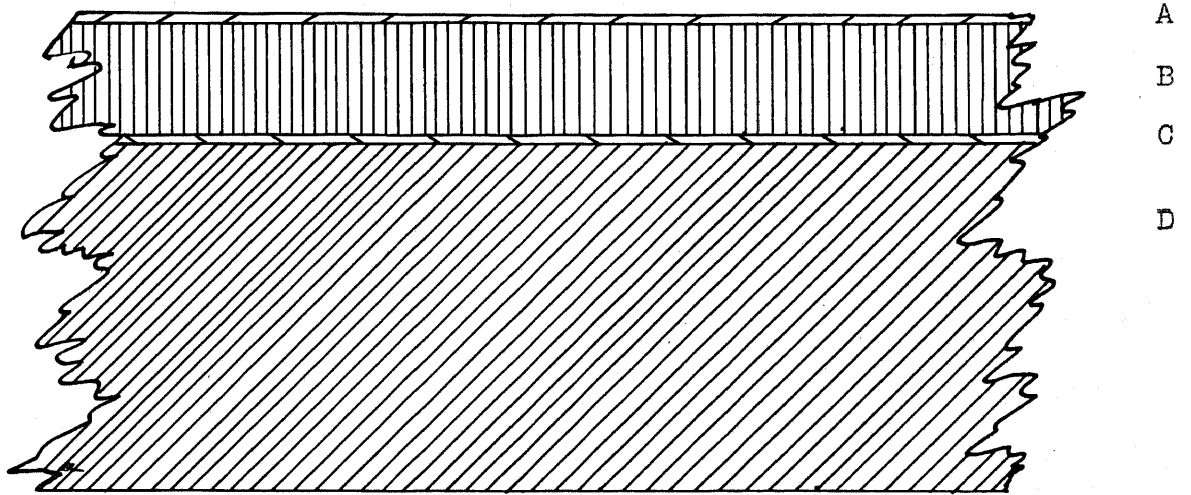
A Cuprous Oxide Disk,
illustrating the characteristic
warping found after the heat-
treatment. The full view is
shown to a reduced scale.

With this background of fact we can now enter into another discussion and see what peculiarities we had discovered as we were following the general trend which lead to our final results. There are many of these, some common to both good and bad units, and some to one or the other. Some little mention of characteristics has been made with especial reference to the microscopic appearance but there were many others.

Perhaps, the first distinct characteristic noted is the curvature that all disks possess. This effect is the rule regardless of the position of the disk during heating. It was first thought to be caused by a drooping of the copper at elevated temperatures, but even when disks are heated back to back with their axes vertical the curve was identical to both. Nor does this curve exist prior to the quenching as inspection shows. This, then is an effect directly attributable to the quench and to be explained in like terms. Of course, the obvious was unequal contraction of the copper and cupreous oxide but of this more anon.

The next peculiar point was the cracking of edges of oxide both on the inside and on the outside of the washer shaped disk. This was covered in a previous comment but again is a function of the quench and possibly of contraction conditions.

The next point lay in the copper coating redeposited on the oxide surface. As a routine, this was always polished before the unit was tested, but we discovered the amount of polish as well as the thickness of the copper had their effects. The best rectifiers were those with the least amount of copper, providing that the coat was uniformly and completely distributed. A partial



- A - Redeposited copper on surface of disk.
- B - Layer of Cuprous Oxide.
- C - Intermediate Layer (Possibly does not exist)
- D - Body of copper disk.

A Cross-Section of a Rectifying Disk.

explanation was attempted by saying that the redeposited copper had a resistivity much higher than that usually assigned to copper. There is a real truth here, in that, by our observations the copper had a soft surface and a spongy texture showing that a solid coat was not effected but that the copper retained to a degree the skeleton lattice of the oxide crystals from which it was reduced. There was more though than this. A heavily coated unit, even after a partial stripping did not give as good results as a unit less heavily coated during quench.

Electrical tests showed even more peculiar reactions than the mechanical phenomena. Some of the interesting types of units encountered cannot be explained yet, and others lend themselves to the general theory we developed. The first noted variation from the orthodox was the effect that we called colloqually "crawly backs", and a very concise term it is. As the reverse current was read the pointer of the milliammeter would take an initial position at a fair value and then slowly but surely it would work up the scale, sometimes stopping at a value several times the original point after some moments, and sometimes continuing up the scale until the breakdown of the resistance was indicated. Some of this we believe was caused by leakage currents around the edges, and this is accelerated if the unit has any moisture on it, some of it we found to be caused by the chipped edges themselves, apparently without any moisture present and some we attributed to a gradual let-down in the very oxide of the unit.

As an example of the second point, I can cite instances where, after testing, the edges were chipped further and the reverse

current exhibited an increase on subsequent testing. An incidental result of this work lead us to larger units to reduce the ratio of edge to area and this we found beneficial in one view. But another point entered, the forward current, which did not increase at all in proportion to the area increase and so this was discarded.

A parallel to the "crawly backs" was the condition called "crawly forwards" which exhibited the same characteristics when the forward current was measured as did the other when the reverse was read. These were, for the most part, due to leakage and to chips of copper clinging so as to short between disk copper and top copper.

Another peculiar type was called "pressure back" because it showed a different resistance for every different pressure applied. This was a distinct and different phenomena from the one previously discussed but sometimes both effects were noticeable in one disk. This type would return to its initial value the instant pressure was relieved, whereas, the other took an appreciable time lapse before its initial reading became the same as it had been previously.

As for microscopic peculiarities, these were covered in our previous discussion but in reiteration they were: the secondary mottle, the pitting and the thickness of the primary mottle, all conditions of the bottom copper, as well as the size and shapes exhibited by the crystals themselves. The desirable features we have discussed, and it was impossible to credit any variable factors very definitely as caused by any one peculiarity.

It remains then to discuss the disks connected in the bridge and their reactions. It was found that these reactions did not differ greatly from those of a single unit. It may be advisable in discussing the bridge connection to refer the reader to the voltage wave shown in the Mathematical Appendix and to point out that a rather severe strain is put on the unit when the battery and A.C. wave are additive. This means that the back voltage to which the unit offers high resistance is greater than the forward voltage in the ratio of the sum of the battery voltage and peak A.C. voltage to the difference between the peak A.C. volts and the battery E.M.F.

There are certain tests which can best be performed with the completed bridge and among these the life tests on various types of units are most interesting. After a gradual drop over some days the current output and the efficiency stabilized and did not change further over extended periods of time, provided that the units comprising the bridge were not too badly chosen with regard to the back and forward resistance and that the "erawly" and "pressure back" type were avoided.

Another interesting test lay in the temperature runs made with variable surrounding temperatures. A low value increases the output greatly and a high output decreases until it is possible to cause the complete reversal of the direction of rectification. And a further heating (to 80° C) was found to destroy the efficacy of the unit permanently, or at least to impart its useful life materially.

The most interesting section of our work lay undoubtedly in our surmises on the cause of the rectification that occurred when we treated cupreous oxide in the prescribed manner.

To understand what was happening, we went to texts and authorities to see what were the accepted theories of crystal rectification and to see how completely they answered our conditions. We found many explanations for the purely crystalline rectification, but nothing that could help our work. As a brief review, we can say that the effect of rectification discovered by Dunwoody (1906) and patented in his name has been studied by Pierce (1907) who holds for "point contact" rectification, Eccles (1910) who explains by thermal variations due to the Joule effect. The present attitude is for the most part that rectification is due to a unilateral conductivity, so that when alternating current is applied, the resulting mean current is a function of the alternating voltage (Dictionary of Applied Physics iip. 647 - 1922).

In addition J. Strachan (Wireless World XIV P-245 - 1924) explains by giving the molecules axes of conductivity, polar in nature and reversible. At the point contact (which is the only type he attempts to explain) the molecules actually move so as to convey current for one-half the cycle and impede its flow the other. A.C. James reviews the electrolytic theories and adduces experimental data with especial notice of temperature effects. In his conclusions he says, "Unilateral conductivity and rectification can be explained from consideration of the structure of crystals and by the fact that in solid electrolytes the current is carried entirely by one set of ions, the other set forming the fixed framework. In rectification, the metal ions oscillate to and fro through

fixed channels of sulphur ions, giving metallic and non-metallic contact alternately".

Grondahl explains this theory of cupreous oxide rectification by space charge effects just as one would explain the rectification of a vacuum tube. He says, in the article referred to previously (A.I.E.E Journal) that the ions are free to migrate from oxide to copper (parent) and that they are ever present and that when an alternating voltage is applied the ions can drift across this boundary without undergoing the full potential drop which might be expected to occur.

Our experimental work was essentially practical in its nature, and therefore, we cannot point to minute fragments of evidential nature relating to ionic drifts but we have formed some few definite conclusions which may prove of interest, if not of some scientific worth.

We must first accept the fact that cupreous oxide, per se, rectifies. This is definite. (As for why this occurs we cannot say much except that it appears to be a process which takes place within the crystal and throughout the entire crystal, and not limited to surface or point. Next we can only assume that the space lattice is such that conduction can take place in one direction only. This may be an effect such as reflection and refraction of light waves but we have nothing definite to which we can point.

The fact to which we can point definitely is that pressure applied normally to the plane of rectification will increase the ratio of forward to reverse resistance. Let us consider some of our experimental data. Pressure, we know is present, due to the

cracking off of the chips, as well as to the warped condition of the unit, developed, as we pointed out in the quench and not before. That it is great is also sure. This pressure is developed by the shrinking of the copper and the cupreous oxide at different rates, leaving the oxide in compression and the copper in tension. Sometimes the strain will become so great that the oxide will lift off the copper--strip away entirely in spots although held in relative position by other adherent portions. This condition is productive of the "pressure forwards" of which we have spoken. As we applied pressure, the oxide came into more intimate contact, as well as becoming compressed more greatly. Both of these increase the current, and in direct ratio. Grondahl's ionic drift theory can hardly be extended to rectification occurring through air spaces at normal temperatures. And this lifted condition is clearly visible to the unaided eye.

We can also point out that there exists definite pressure concomitant to greatest rectification ratio, and that above and below this pressure the ratio is not as good. Let us examine the curve marked "Time in Air" after First Furnace Treatment" in the light of this view of pressure. A critical point we find, for greatest ratio and a quick cooling which prevents us from quenching at exactly the correct time (or temperature or pressure as you will) and an indeterminate maximum point. When we come to the two furnace method we find the curve modified and the current a rounded curve of greater distinctness and a clearly defined optimum condition. We gain time for seasoning the stresses attending the first cooling, and then we quench from the temperature which will produce the correct pressure for our work.

As a further demonstration we can consider the effect of temperature changes on the completed units. An increase of temperature decreases the output as the pressure is reduced. It is true that a decrease of temperature increases output but we have not reduced temperatures far enough to be sure this is consistent. According to our theory, the rectification should be poorer as the temperature becomes materially lower, but no experimental work was done lower than freezing point.

CONCLUSION:

There is an attraction to research which is hard to define. My conclusion can point to nothing more definite than certain approximations of the truth as we see it in connection with our work and these are summarized on the preceding pages. In this section I would rather generalize and consider the work from a personal point of view. To realize what has been accomplished is not as great, from the personal view, as the realization of what the person himself has had to learn in order to gain the result.

We had to school ourselves in that first precept of any investigation, patience, and not a patience of minutes over petty delays or hours over some small point. We found that days and even weeks were required to solve some particular item to any satisfaction. Patience and application were then the first requisites.

Next and allied to the first point, we found that a rational concept of what we wanted, and how we were to proceed were required. Purpose and directed purpose was a necessary aim and in the work we soon found something that deserves a full section, yet properly comes under "purpose".

Stated baldly it reads, do not change more than one factor at a time. In our work and work of similar nature, this cannot be ignored. For we sought exact solutions and it is impossible to attain accuracy where the method is inexact. Many the time we have attempted to vary a single factor, too, only to find that

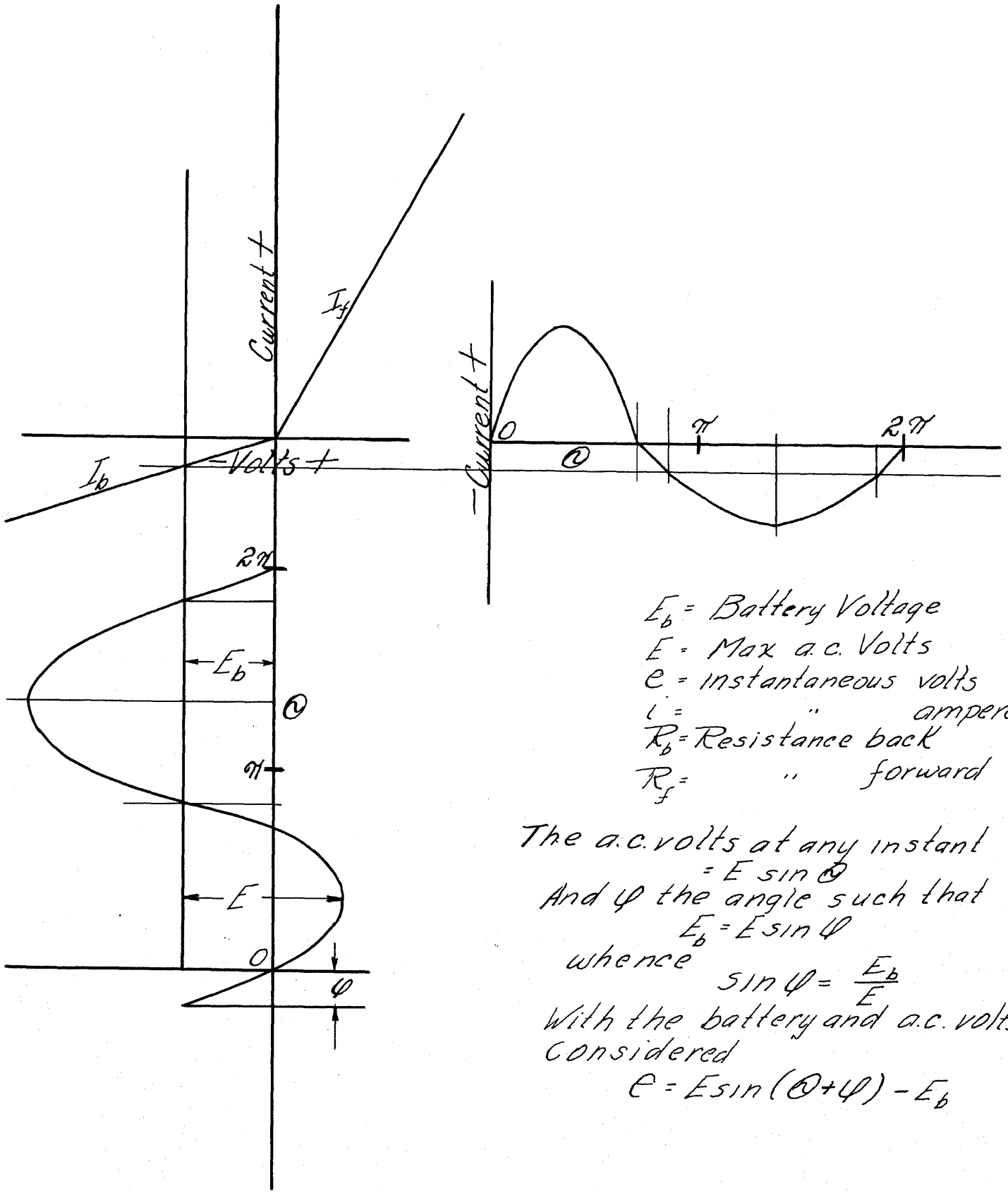
unconsciously or unknowingly we were affecting another at the same time. So one must know all the factors, know which one he wants to vary, and then do so with the minimum of disturbance for those other related effects. One cannot vary furnace atmosphere in a gas or electric muffle without guarding against a change in furnace temperature, nor can one expect results any more accurate than the accuracy of the instruments, mental as well as physical, that are brought to bear on the problem.

An accuracy, then, of thought as well as an accuracy of manipulation--and a mind capable of interpreting results in their true lights rather than in misleading fashion. Research workers may be born to it but one can certainly add that they need much training before their aptitude becomes apparent.

There is one point worth leaving to the last. And it is the only point that can ameliorate completely and fully the foregoing. It is the thrill of solid accomplishment and of the knowledge of a task well done--if it be only a small factor in an entire problem. One can feelingly know that here is his bit for the world's store of information--here is his reason for being and his gift to humanity.

The richest and fullest life is that life which reaches out, affects many for their good and the palm of this modern day rests certainly in the hands of those workers whose lives seem coldly remote from affairs. They are the richest of mortals in spiritual possessions.

On the following pages will be found a derivation for the current values found in a rectifier of characteristics such as we are using. It is to be noted that the forward and reverse current resistances are considered as constant for all values of voltage, and assumption that is not absolute. The effect of inductance has also been neglected, as it is generally low.



- E_b = Battery Voltage
- E = Max a.c. Volts
- e = instantaneous volts
- i = " amperes
- R_b = Resistance back
- R_f = " forward

The a.c. volts at any instant
 $= E \sin \theta$

And ϕ the angle such that
 $E_b = E \sin \phi$

whence $\sin \phi = \frac{E_b}{E}$

With the battery and a.c. volts
 considered

$$e = E \sin(\theta + \phi) - E_b$$

To determine the area of the positive (charging) wave,

$$[i]_0^{\pi-2\varphi} = \frac{E \sin(\theta + \varphi) - E_b}{R_f}$$

and the area $\int_0^{\pi-2\varphi} i d\theta = \int_0^{\pi-2\varphi} \frac{E \sin(\theta + \varphi) - E_b}{R_f} d\theta$

Solving:

$$= \frac{E}{R_f} \int_0^{\pi-2\varphi} \sin(\theta + \varphi) d\theta - \frac{E_b}{R_f} \int_0^{\pi-2\varphi} d\theta$$

$$= \frac{E}{R_f} [-\cos(\theta + \varphi)]_0^{\pi-2\varphi} - \frac{E_b}{R_f} [\theta]_0^{\pi-2\varphi}$$

$$= \frac{E}{R_f} \{ \cos \varphi - [\cos(\pi - \varphi)] \} - \frac{E_b}{R_f} (\pi - 2\varphi)$$

$$= \frac{E}{R_f} (\cos \varphi + \cos \varphi) - \frac{E_b}{R_f} (\pi - 2\varphi)$$

$$= \frac{2E}{R_f} \cos \varphi - \frac{E_b}{R_f} (\pi - 2\varphi)$$

From construction;

$$\cos \varphi = \frac{\sqrt{E^2 - E_b^2}}{E}$$

and $\varphi = \sin^{-1} \frac{E_b}{E}$

Substituting,

$$= \frac{2E}{R_f} \cdot \frac{\sqrt{E^2 - E_b^2}}{E} - \frac{E_b}{R_f} (\pi - 2 \sin^{-1} \frac{E_b}{E})$$

$$= \frac{2\sqrt{E^2 - E_b^2} - E_b (\pi - 2 \sin^{-1} \frac{E_b}{E})}{R_f}$$

To determine the area of the negative (discharging) wave

$$\begin{aligned}
 \int_{\pi-2\psi}^{2\psi} i d\theta &= \int_{\pi-2\psi}^{2\psi} \frac{E \sin(\theta + \psi) - E_b}{R_b} d\theta \\
 &= \frac{E}{R_b} \int_{\pi-2\psi}^{2\psi} \sin(\theta + \psi) d\theta - \frac{E_b}{R_b} \int_{\pi-2\psi}^{2\psi} d\theta \\
 &= \frac{E}{R_b} \left[-\cos(\theta + \psi) \right]_{\pi-2\psi}^{2\psi} - \frac{E_b}{R_b} \left[\theta \right]_{\pi-2\psi}^{2\psi} \\
 &= \frac{E}{R_b} \left[-\cos(2\psi + \psi) + \cos(\pi - 2\psi + \psi) \right] - \frac{E_b}{R_b} \left[2\psi - (\pi - 2\psi) \right] \\
 &= \frac{E}{R_b} (-\cos 3\psi - \cos \psi) - \frac{E_b}{R_b} (\pi + 2\psi) \\
 &= \frac{2E}{R_b} (-\cos \psi) - \frac{E_b}{R_b} (\pi + 2\psi)
 \end{aligned}$$

Again Substituting,

$$\begin{aligned}
 &= \frac{2E}{R_b} \left(-\frac{\sqrt{E^2 - E_b^2}}{E} \right) - \frac{E_b}{R_b} \left(\pi + 2 \sin^{-1} \frac{E_b}{E} \right) \\
 &= \frac{-2\sqrt{E^2 - E_b^2} - E_b \left(\pi + 2 \sin^{-1} \frac{E_b}{E} \right)}{R_b}
 \end{aligned}$$

THE Total Area, then, is

$$\frac{2\sqrt{E^2 - E_b^2} - E_b \left(\pi - 2 \sin^{-1} \frac{E_b}{E} \right)}{R_f} - \frac{2\sqrt{E^2 - E_b^2} + E_b \left(\pi + 2 \sin^{-1} \frac{E_b}{E} \right)}{R_b}$$

The average I is found by dividing the equation above by 2π .