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Title: MERCURY RECTIFIERS

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SECRET

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TECH

INTRODUCTION

The manufacture of high-vacuum-proof current leads for iron rectifier vessels was carried out by AEG according to a specially developed hard soldering method. The same method was later taken over by the Rectifier Bureau, and was used, on the whole, unchanged, until the beginning of 1948. The first summary of the method was presented at the end of 1945 in the following reports:

Rg 102 a: "The structural elements of high-vacuum-proof current leads and their manufacture"

Rg 102 b: " The vacuum soldering method of vacuum-proof current leads"

Rg 102 c: " Testing method and testing apparatus used in the manufacture of high-vacuum-proof current leads".

The setting up of a new basis for the manufacture of leads by the rectifier bureau in 1946 and 1947 resulted in the publication of a final report, supplemented by practical experience and a large number of drawings:

Rg 119 : " The manufacture of high-vacuum-proof hard-soldered current leads".

Development continued. Occasional breakdowns, and increased use of materials necessitated an early investigation of all problems of soldering (cf. report Rg 118 "The state of the experimental work on hard-soldered current leads"). The work yielded major successes only after a new method of soldering, the electrolytic vacuum soldering method, had been introduced. The results of manufacture by this method, which has been in use for quite some time have shown its advantages. The description of this process, as part of the over-all manufacture process, is the subject of this report. The data of report Rg 102 a on form and assembly of the parts of the lead apply unchanged to the electrolytic soldering method, and are not repeated in detail in this report. The report, however, is prefaced by a short summary of the development and by a detailed description of some features which were not stressed in previous reports to the extent which seems desirable in connection with the electrolytic soldering process. These are, especially, directives for the forming of the soldering point and data on the chemical structure of the ceramic materials employed.

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The Issue of Hard-Soldering of Vacuum-Proof Current Leads Made of Frequenta

A. General Considerations.

In contrast to other hard-soldering methods, whereby ceramic surfaces are produced which can be soldered by employing intermediate layers of sintered compounds of heavy metals, e.g. wolfram oxide or titanium hydride, the AEG method was the first one to connect directly the natural surface of the ceramic substance with the soldering metal. The choice of the known ceramic insulation materials was limited, especially when it is borne in mind that the requirements included, in addition to the soldering ability, also vacuum-proofness of the unglazed material, high stability against temperature changes, and sufficient mechanical strength. Under those conditions, the choice fell on a material known in high-frequency technique by the name of Frequenta. Investigations of condensers with silver-coated Frequenta plates by other researchers established that the silver will migrate into the ceramic dielectric. In fact, the first soldering experiments which were carried out in a vacuum in order to establish flawless contact between solder and Frequenta accomplished solid connection between both substances and confirmed the diffusion of the silver. As for the other specifications, Frequenta met the requirements fully; its use as an insulating intermediate element subsequently led to a practicable design of lead.

The most simple type of such a lead consists of a ceramic hollow cylinder with one metallic connecting piece each SOLDERED to the discharge vessel and to the conductor running through the hollow cylinder. These connecting pieces are soldered NOT to the vacuum-proof to the cylinder. Figure 1 shows the practical design of the lead according to the AEG method. Concentric iron sleeves are placed around both ends of the Frequenta tube. The lower, longer sleeves serves for the connection NOT of the lead with the discharge tube, this connection to be established later; the upper short sleeve, welded to an iron plug, is the head of the lead and at the same time the HOLDER FOR the internal conductor. The conductor is fastened to the plug by means of threaded pins, if the lead is small; if the lead is large, it is welded to it.

In developing of the standard design as shown in Figure 1, special attention was given, in addition to the construction features, to the difference in the

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coefficients of expansion of Frequenta and iron. The linear expansion of iron under the influence of heat is about thice that of Frequenta. This means that, in case of change of temperature, stresses will occur in the material, and their effect on ceramic and solder must be reduced to remain within tolerable limits. Despite its very great expansion, the pure silver which is used as solder hardly takes an active part in the setting up of these stresses; however, its plastic deformability is an important factor for the compensation of stresses between the sleeves and the Frequenta. The tensile strength of the Frequenta is approximately 900 kg/cm^2, while its compression strength is 10,000 kg/ cm^2. In other words, it is twenty times more sensitive to stress than it is to pressure. In the type of lead designed, this fact has been considered. The position of the soldered point at the external circumference of the Frequenta tube, the contracting force of the iron sleeves during cooling will affect the ceramic material mostly as tangential pressure, while the tangential stress simultaneously occurring in the iron will be absorbed by partly permanent and partly elastic changes of form of the sleeve. At room temperature, the silver-Frequenta system is subjected to considerable, but not excessive pressure which is reduced during heating and turns into stress after the elastic deformation of the sleeve has ceased. The maximum heating or operating temperature of the lead depends to a great extent on the tensile strength of the ceramic material and of the soldered point, or on a more or less effective reduction of the stresses by proper design of the portion of the sleeve in the immediate vicinity of the soldered point.

On the basis of these considerations, the sleeve portion around the ceramic material was given the shape shown in Figure 1. Between the two guide edges for the Frequenta tube, the sleeve is turned down to a mechanically permissible wall thickness; in the middle of the hollow space thus formed, sleeve and Frequenta are connected by the solder. The bulge shown in the picture as soldering space is thus formed of the soldering zone, and an outer and an inner hollow space. Because of the floating arrangement of the silver rings, the pressures and stresses already held down to a minimum by the thinness of the wall of the sleeve are no longer affected by the continuation of the sleeve, which is thicker for reasons of stability. The walls of the sleeve, acting like membranes, above the hollow spaces, allow the soldered point to "breathe" without difficulty during change of temperature.

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This applies, however, only under the condition that the solder metal is really connected to the sleeve only within the strip called the soldering zone. For this reason, the areas of the sleeve which close off the internal and the external hollow space are coated with a paste made of toluene, polystyrene, and talcum. In heating, the polystyrene is depolymerized to form styrene, which will evaporate as a neutral hydrocarbon together with the toluene and is drawn off by the pump, leaving behind a whitish layer of talcum which is sufficiently adhesive and which will prevent the liquid silver from wetting the area.

This coating, together with the molecular forces of the liquid solder, causes a capillar depression opposed to the forces of gravity. This capillar depression will drive the solder into the soldering zone under little pressure and will maintain it afloat there. If the pressure which is required for flawless soldering is to be maintained , the amount of solder in the soldering space must be bigger than can be absorbed by that space . The upward force is a product of the vertical component of the surface tension of the liquid solder and of the length of the unwetted line of contact between coating and solder. The effect of this upward force is contingent on the solder not reaching the lower limit of the soldering zone; it will be greatest when the solder protrudes into the hollow space underneath the soldering zone, all along the circumference of the sleeve. A liquid ring of silver whose volume corresponds to the volume of the wetting soldering zone remains afloat when part of its height does not protrude into the not wetting hollow space, until the vertical component of the surface tension is in equilibrium with the force of gravity of the liquid solder. This portion of the silver ring will be lost to the soldering zone. At least the same amount of silver must be added to each solder point as reserve in advance, if flaws in the solder ring are to be avoided.

On the upper edge of the soldering zone, capillary force and gravity exert effects which are both directed downward, and the sum of these forces will be at least in equilibrium with the force acting upward. Thus the solder which has flowed properly is characterized by an upper edge which is straight along the uppermost limit of the soldering zone, while the lower edge is irregular and usually hangs down spy below the lower limit of the soldering zone. This hanging solder, the so-called reserve, is held so far away from the sleeve wall by the

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non-wetting coating, thereby the membrane effect is not affected.

B. Frequenta

Of the three elements of a lead (iron, silver solder and Frequenta), the Frequenta is the most important. Solder connections between silver and iron are, of course, easy to produce, and by maintaining their degree of purity, their quality can be maintained at a constant level. Soldered connections between silver and Frequenta, however, are not so easy to produce, since one of the materials is a plastic, and these soldered connections depend on structural and chemical prerequisites, if they are to satisfy the requirements of being vacuum-proof and insensitive to temperature within certain limits.

Frequenta is a material made predominantly of magnesium silicate-containing masses. In the standards DIN 40685 it is assigned to group II B, a special steatite mass. According to the data supplied by "Steatit", the manufacturer, the original Frequenta is produced by wet grinding of the following components:

87 % by wt. of Coopferasgruen steatite

8 % by wt. of barium carbonate (witherite)

4% by wt. of Wildstein blue clay

1 % by wt. of calcium carbonate.

An average analysis of the steatite used shows the following pictures:

60.3% SiO_2

31.3% MgO

1.4% Al_2O_3

1.4% Fe_2O_3

5.6% volatile matter

Thus, the average composition of Frequenta is:

58% SiO_2

27% MgO

8% BaO

6% Al_2O_3

1% Fe_2O_3

During the first period of development, the more basic reasons for the fact

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that Frequenta can be soldered were not understood. Because it is very difficult to analyze ceramic materials, the best soldering conditions were developed experimentally. At first, the tests were made with ground Frequenta tubes, usually greenish-gray in color, burned by Steatit with the exclusion of oxygen, and brought on the market under the name of "Frequenta AS 42". While soldering with those tubes was satisfactory on the whole, attempts were made at the same time to improve the process. Exact evaluation of a greater number of soldering tests showed that some tubes whose color was not the same as that of the others, but yellowish brown instead, gave especially good results. Steatit, when asked for the reason of the difference in coloration, stated that the yellowish brown tubes had come in contact with oxygen during the burning. This fact turned out to be of importance for the future investigations.

According to Schusterius and Baessler, Frequenta is a mass of intergrown magnesium silicate crystals which are attached to each other by glass flux. In the crystal grid of the magnesium silicate, the iron is either deposited in metallic form, or as an oxide. Whether the metallic iron or the one of its oxides are prevalent in the basic material cannot be stated definitely, but it can be assumed that most of the iron is in the form of Fe_3O_4. This ferric oxide of the basic material remains unchanged as long as burning takes place in a neutral or in a reducing atmosphere. The external characteristic of such tubes is their greenish-grey color. The creating of a soldered connection with silver is probably due to the fact that when the material is heated under a vacuum, part of the Fe_3O_4 on the surface of the Frequenta will be reduced to iron bound to the ceramic. The metallic component allows the attachment of silver atoms. This assumption is further borne out by considering the qualitatively superior soldering with Frequenta tubes which had been burned in the presence of oxygen. When the tubes are burned in an oxidizing atmosphere, the Fe_3O_4 of the Frequenta mass is transformed by the ample supply of oxygen into the higher stage of oxidation, Fe_2O_3. The external sign of this oxidation process is the change of coloration to yellowish brown, while its effect on the solder connection is that of considerably greater reducibility of the Fe_2O_3 during vacuum soldering.

Reducing burning is naturally more effective on the surface than it is in the interior of the Frequenta mass. A layer of several tenths of a millimeter in

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depth is clearly distinguished both in color and structure from the lower layers. In the course of the experiments, this layer, the so-called burning skin, gave good soldering results. However, the burning skin is lost by the subsequent grinding. It was agreed to have Stemag perform an oxidizing second burning at a temperature of 1230 to 1240°C, called muffling. The material burned in an oxidizing atmosphere, then ground and then muffled was given the designation "Frequenta AS 42 burned under oxidation". As the material was finally only produced by this process, its name was shortened back to "Frequenta AS 42".

The good results during the first years of manufacture obtained with AS 42 tubes were reduced in quality for the first time during the war, by a change in the material which was at first beyond control. Similar setbacks occurred when the production of electrical leads was resumed by the Rectifier Bureau. Stronger generation of gas at the surface of the Frequenta, and general reduction of the soldering ability of the material have caused considerable waste due to rejection when production was started again.

The reduced soldering ability was attributed to the lack of iron oxide. To eliminate this shortcoming temporarily, the soldering zones on the finished Frequenta tube were coated with a thick solution of iron hydroxide and annealed in air for several hours at 1230°C. The method by itself was feasible, but due to the difficulty of proper agreement between annealing time, speed of diffusion, and the quantity of the iron hydroxide layer to be applied, and due to the laboriousness of the second annealing process, it was dropped again. At the beginning of 1947 an agreement was made for the first time with Stemag on the addition of artifical iron oxide quantities to the Frequenta raw material. These experiments led to the "Frequenta AS 42 G", burned under oxidation and muffled, with an added iron oxide content of 1.5%, which was to ensure good soldering properties independently of the oxide naturally present.

C. The Causes of Poor Soldering Ability:

The first test solderings carried out on leads with the new AS 42 G material were successful and promising (cf. report Mg 118). However, the subsequent tests again brought setbacks, and it was realised that the initial success had been accidental and that increase of the iron oxide content alone does not guarantee

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good soldering. Before we discuss the reasons for this failure in detail, a short explanation of the evaluation of soldered connections is required.

Good solder connections have higher tensile strength than the Frequenta itself. If the sleeves of usual wall thickness are cut open and unwound in the manner a certain manner, they will tear off inside the ceramic material, and the silver solder strip which is ripped off together with the sleeve will be covered with a thin layer of ceramic material which shows fine cracks. With some experience, the appearance, the distribution, and the quantity of Frequenta which remains attached to the silver give a good indication for of the quality of the soldering job.

During the first period of production, when AS 42 was used exclusively, three causes of waste were observed. In addition to waste due to faulty manufacture which was avoidable. These causes of waste were poor soldering quality which does not necessarily cause poor connections. It can generally be recognized by the fact that the silver surface which has been unwound from the tube will be covered only incompletely with remnants of the ceramic material and that these remnants are easily dissolved. Leads of this type will usually pass the first temperature test, but in operation their life is short, because the constant thermic stresses will eventually cause the soldered connection to become loose.

Even already during the first period of production, the main cause of rejection was the generation of gas at the surface of the Frequenta. The Figures 2 and 3 show the effect of this gas on the silver. These figures each show one characteristic section of a cut sleeve which has been unwound from the Frequenta tube and bent straight. The height of the pictures is approximately the same as the length of the bulge of the sleeve, or the height of the soldering space. The soldering zone is located approximately in the middle third of the picture. Its upper limit is marked by the horizontal edge of the silver, while the lower one is obscured by the silver reserve which hangs down below it.

The silver surface shown in these pictures is broken up by numerous cavities, which are gas bubbles, and which in some places are so numerous that the sealing silver surface is reduced to a fraction of its original width. The strength of the connection at these points is accordingly low and the longevity is reduced correspondingly. Under especially unfavorable conditions, the gas does not collect in

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sharply defined cavities, but forms thin films on large parts of the surface of the Frequenta, thus completely disrupting contact with the solder. The silver then does not show the impression of the ground Frequenta surface, characteristic for good solder connections, but it represents a picture which can contain all manifestations of unilaterally unimpeded crystal growth. The surface is frequently divided into a network of irregular crystals by faintly showing grains, (similar to the structure of slightly etched metals), it is or it is covered by a relief of freely solidified crystalline ribbing(Fig 3). The same crystalline ribbing can also be recognized in the cavities in Figures 2 and 3. The appearance of such gas films almost always causes the leads to be leaky.

The third cause of waste is a peculiar property of the silver. Silver is able to absorb considerable quantities of oxygen, depending on the temperature. The absorption capacity for oxygen changes suddenly as soon as the change point has been ~~xxxxxx~~ passed. Thus, at the instant of solidification, a large percentage of the absorbed oxygen will suddenly be released. During the cooling of a lead, the silver never solidifies simultaneously all along the circumference. Should a small amount of oxygen have been absorbed during the beginning of cooling, this amount will migrate into the still liquid metal adjacent to the metal which is beginning to solidify and will thus increase the oxygen content there to an even higher percentage. By this manner, the last ~~xxxx~~ liquid remnant of the silver will have an increased oxygen concentration, and this oxygen will be released with increased suddenness at the moment of solidification and will give rise to the formation of cavities broken up by dendritic crystalline structures within the solidified silver. This process is known by the term of "spitting". Spitting causes fine cracks, some below and some on the surface, usually running in a lateral direction. Waste due to spitting cannot be completely eliminated at the present state of soldering technique, but a proper vacuum and nitrogen for the oven, which contains as little oxygen as possible, can keep the waste due to this phenomenon down to a tolerable 2 to 3 per cent.

These causes of waste can of course occur simultaneously. It is sometimes impossible to determine whether the creation of a cavity ~~xxxxxxxx~~ filled with dendritic crystals is to be attributed to a gas bubble or to spitting. Even small impurities, such as grains of talcum, can cause large crystalline rough spots on the surface of

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the silver, as is shown in Figure 3.

The occurrence of waste due to the first phenomenon described coincides in time with the use of the Frequenta AS 42 which had a low iron oxide content. Similar difficulties did not occur with the AS 42 G. Even then, the numerically greatest portion of the waste was due to faulty soldering caused by release of gas and by spitting. MOST of the oxygen-containing gas is to a large extent the oxygen liberated at the surface of the Frequenta by the reduction of the Fe_2O_3. (Note: This last sentence is garbled in the original and does not make sense. This is only an approximate translation and may not be correct.) No ideal conditions could be attained despite the improvements introduced. For reasons of economy, the removal of gas from a soldering furnace cannot be carried out to any desired degree, and it is therefore understandable that the results with the well-soldering but oxygen-rich AS 42 G were not sufficiently free of bubbles even after a soldering time of one hour. The occurrence of spitting is of course tied up with the release of oxygen from the Frequenta, because part of the liberated oxygen will be eagerly absorbed by the molten silver. At any rate, it was possible to keep the rejects within an economically tolerable limit, until the electrolytic soldering method was introduced. Figure 4 shows a typical example from this transition period. The individual gas bubbles in the upper portion of the silver surface which is covered by a solid layer of AS 42 G, and the two larger cavities in the silver reserve which is hanging down (lower left on the picture) do not have much effect on the quality of the soldered connection. However, there is always the danger of an accumulation of bubbles which by itself or in conjunction with spitting may cause leaks.

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The Electrolytic Hard-Soldering Method

A. The First Electrolytic Soldering Experiment

At the time when it was realised that Frequenta AS 42 C cannot fulfill all requirements because it gives off oxygen too violently, and that the present method offered little chance of improving the quality, the development was turned onto an entirely new path by a novel idea.

It was known that ceramic insulation materials become conductors of second order, if sufficiently heated. An electrical effect on the soldered connection thus seemed possible. The conductivity in this case is of an electrolytic nature; the current takes place by migration of ions, and depends on the degree of dissociation of the heated ceramic electrolyte and on the mobility of the ions. The first item to be tested for its suitability was the most commonly used lead with a diameter of the Frequenta of 29 mm. The specific resistance of standard Frequenta, as given by Steatit, was used as basis for a rough calculation. This calculation, assuming a temperature of 1050°C and an electrolysis voltage of 200 to 300 V, showed that the passage of a current of several milliamps might be possible.

The first preliminary experiment in 1947 was based on the idea that thermo-ionised silver atoms at the surface of contact between silver and Frequenta might be made to migrate into the ceramic material if a direct voltage were applied. An already soldered, faulty lead made of AS 42 was placed upright on the iron base in the vacuum furnace and the head of the lead was connected with an iron wire which, for purposes of insulation, ran through the rubber sealing of the observation window. The lead was kept at a temperature of 1057°C on the average, for 60 minutes. During this time, a 260 V direct voltage was applied through an ammeter and a 10-ohm protective resistor, so that the head of the lead represented the anode. The electrolytic current of about 5 mA, which appeared, corresponded approximately to an electrode current density of 0.9 mA per sq.cm.

If it had been expected that the positive silver ions would migrate from the anode into the Frequenta and solidify the soldered connection at that point, the result of the experiment turned out to be a surprise.

The ceramic contact surface underneath the anode was coloured dark brown to a depth of 0.2 mm and spotted; the connection with the silver was poor and the

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silver contact surface was covered by bubbles and spits. However, the ceramic contact surface underneath the cathode was evenly black in color to a depth of about 0.05 mm and the areas enclosed by the two hollow spaces were colored dark to light grey. At these points the entire silver contact area was covered with Frequenta which had torn loose; the solder connection thus was very good. Bubbles or spits were almost completely missing.

This experiment was repeated a few times, until all doubts about the observations first made had been dispelled. It was obvious that the effect had been the opposite of the anticipated one, and that the theory of an active participation of the silver ions in the transport of current had become untenable. The experiment did have one important positive result, because it could be proved that the quality of the solder connection on the cathode side had been greatly improved. It was now possible, with the aid of electrolysis, to fight effectively against the release of gas from the ceramic material. In addition, it could be assumed that the electrolysis had improved the soldering qualities of the Frequenta, because of the black enamel-like layer attached to the silver. That meant that the stocks of AS 42 could be considered, under these circumstances, as fully satisfactory material.

B. Auxiliary Electrode, Lines of Flux and Resistance

The further investigations of the nature of the electrolytic soldering method were tied up with a condition which, at first glance, seems to be of subordinate importance, but which had to be properly fitted to the reaction it had to perform and which contributed not inconsiderably to the success of the project.

Each load has two soldered points which must be treated alike in electrolysis, i.e. they must be connected with the negative pole of the voltage source. That requires an additional electrode for the positive connection, the so-called auxiliary electrode. With the existing design of loads, two areas of the Frequenta tube are in principle available for the auxiliary electrode, the outer or the inner surface between the sleeves. At first, a suitable material for the electrodes had to be chosen. Auxiliary electrodes were made of grains of metal, of liquid metal (silver), and of coatings of powdered graphite. The graphite electrodes was proved in all experiments to be the best solution, not only as far as contact with the ceramic material is concerned, but also in some other aspects which will

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be dealt with later on.

The external electrode shown in Figure 6a, which was used at the beginning, but was soon replaced by others, because of its disadvantages, consisted of a graphite coating applied between the sleeves. This graphite coating was provided with a contact by means of a iron wire which was wound and twisted. The lead was placed into the vacuum furnace in an upright position, the upper and the lower sleeve were connected with each other with an iron wire, and the connection of the auxiliary electrode was carried upward to the observation window, and from there to the outside with insulation.

The interior electrode (Figure 6b) consisted of a graphite coating which covered the entire interior of the [illegible] casing. In this case, the lead was set upside down during soldering and the positive current connection was run through an inserted graphite plug out of the long sleeve and upward. Upper and lower sleeve were again brought to the same potential by means of an iron wire.

The advantage of the interior electrode over the external electrode is obvious by discussing the ease with which it can be connected. The wire connection of the external electrode is difficult to make. In the internal electrode, the place of this connection is taken by a graphite plug which can be used over and over again. This plug is not shown in the schematic sketch. The factor which decided the choice of the internal electrode was the current characteristics within the electrolyte. For purposes of investigating the current characteristics in the wall of the Frequenta tube, potential measurements were carried out in an electrolytic trough which imitated the true conditions. The measuring results are compiled in Figures 7 and 8.

Figure 7a shows the flux lines when an external electrode is used. The chief disadvantage of this electrode arrangement is the unilateral current load on the soldering area, caused by the different path lengths. If an internal electrode is used, the distribution of the current density is very even. Figures 7 b, c, and d show the potential distribution and the current characteristics of a lead with internal electrode [illegible] under three different conditions. Figure 7b is based on the assumption that the sleeve parts which touch and the silver ring will exercise a joint effect on the potential distribution; in Figure 7 c the silver

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ring is the only one which has any influence, while in Figure 7d the influence is exercised by an electrode which is assumed to touch the entire sleeve. As will be pointed out later, none of these three figures represents the actual conditions. The closest approximation of the actual conditions is obtained if the potential distribution is thought to be composed in such a manner of these three possibilities that case 1 will have the greatest and case 3 the smallest share.

For the sake of completeness, another possibility should be mentioned. This possibility, however, has no practical significance at the present moment for the manufacture of leads. It might be of interest, however, for in certain special cases. This possibility is that of influencing the electric field by means of so-called intermediate electrodes which themselves are not connected to the voltage source. It is possible, for example, by means of an intermediate electrode in the interior of the Frequenta tube, to influence the potential distribution of a lead connected to the circuit without an auxiliary electrode (Figure 8a) in such a way that the lines of flux will be nearly vertical on the sintering surface and will be evenly distributed. (Figure 8b). The intermediate electrode will adjust itself to half the voltage

All data on graphite electrodes are based on the assumption that the electrode has a relatively low resistance as compared to the ceramic electrolyte. The following data, on calculated resistances of the common types of leads , and the measured resistances of graphite electrodes should be of value as information on the actual conditions.

The calculated resistance values of the leads are, of course, only approximate values, because the basis of the calculations, the specific resistivity for the two Frequenta masses AS 42 and AS 42 S are not known, and the specific resistivity of a standard Frequenta mass was used instead, the data for this having been taken from a diagram set up by the firm of Steeg (Figure 9). The true value for the above Frequenta masses with a high iron oxide content is probably a little lower. Other factors of uncertainty are the following magnitudes which could be determined only approximately: the average cross-section of the effective range of the current, and the surface of the silver contact area.

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Let ρ be the specific resistivity in ohm per cm, R the external and r the internal radius of the Frequenta tube in cm, then the resistance of a Frequenta ring of 1 cm height will be

$$R_y = \rho / 2\pi \int_r^R dx/x$$

$$R_y = \rho / 2\pi \, (\ln R - \ln r)$$

If the double height of the ring is considered (two soldering points), the resistance of a lead is

$$R_y = \rho / 2h \times 2\pi \times \ln (R/r) \quad \text{ohms.}$$

height

To determine the width of the ring (width of the solder) the average effective diver surface was determined from 10 soldering points which had been cut open. In that case,

$$h = \text{surface} / 2R\pi$$

From Figure 9, ρ was determined to be 1.8×10^{-5} ohm at 1025° C.

Type of lead	R (mm)	r (mm)	ln R/r	Ag surface (cm^2)	h (cm)	R_y (ohms)
16 diam.	8	3	0.98	2.7	1.08	26,000
29 diam.	14.5	8.2	0.57	6.9	1.52	10,700
52 diam.	26	13.75	0.50	16	1.96	7,300
60 diam.	30	19	0.46	19.6	2.08	6,300

The auxiliary electrode is made of fine-grained graphite powder, stirred to a paste with a binder and then applied to the Frequenta surface. For the experiments described here, and for the manufacture, relatively coarse-grained graphite powder was placed into a ball mill with distilled water and ground to a grain size of 5 to 8 $\times 10^{-3}$ mm. The final product, a black, viscous mass, was then dried under slight warming, and then made ready for use. The binder used was the mixture of toluene and polystyrene which was mentioned previously and which evaporates in the vacuum furnace without leaving any residue. The finished paste consists of 150 cc of toluene, 2.5 g of powdered polystyrene, and 53 g of graphite powder.

For the determination of the natural resistance of an auxiliary electrode, a Frequenta tube of 70 mm length and 16.5 mm internal diameter, whose frontal surfaces were also covered with graphite paste, was placed under slight pressure between two fixed graphite electrodes and then heated to soldering temperature

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in the normal manner in the vacuum furnace. Figure 10 shows two of the measuring diagrams. The lower diagram shows the normal resistance characteristics of an electrode made by the above method. The resistance at room temperature is about 600 ohm, but it is reduced to a fraction of this figure (40 ohm) when the graphite grains come closer to one another because the binder has evaporated. In comparison with the resistance of the cesium electrolyte , the resistance of this auxiliary electrode can be neglected. If the proper mixture ratio between graphite and binder is not maintained, the situation can become completely altered. The upper diagram of Figure 10 shows the resistance characteristics of a paste in which the mixture has been broken up by the formation of sediment and which contained too high a proportion of binder. The final resistance here is as high as 1,000 ohm and can therefore not be neglected.

The applied paste film dries quickly and it will not be affected by the further processing. The thickness of the layer to be applied is a matter of estimation; in general, the layer will be sufficiently thick when the surface of the Frequenta is deep black everywhere. When the auxiliary electrode is applied, care must be taken not to apply it further than about 2 mm from the front end of the Frequenta tube in the direction of the head of the lead, to safeguard against glow discharge. On the opposite end, however, it should extend for 1 or 2 mm over the frontal end area(Figure 6b), because most of the transition of current from the line and the auxiliary electrode takes place at that point. The electrical connection is accomplished by means of a graphite plug which sits loosely in the Frequenta tube and which has a narrow protrusion which presses against the edge of the auxiliary electrode. The graphite plug is extended to the edge of the sleeve by means of an iron rod (Figure11).

The graphite electrode has the great advantage that it can be easily removed after soldering. It is washed with a cylindrical brush and carbon tetrachloride and then rinsed with clean carbon tetrachloride. High-voltage tests have shown that this cleaning suffices for the removal of all the graphite. With a washed tube of 70 x 29 x 16.5, crackling occurred between the frontal areas only at a voltage of 28 kv, and external breakdown did not take place until 32 kv had been reached.

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8. Investigations of the Nature of the Frequenta-Electrolysis.

The development of the auxiliary electrode marked the beginning of a period which was introduced by individual experiments, but which was soon carried further, ideally supported by observations carried out on the sizable number of items which were being produced. In discussing the experimental results described in the subsequent chapters and the explanation of the entire complex of questions, which follows, it must be borne in mind that a very difficult and still little known special field was treated here with insufficient means. All investigations were badly hampered by the fact that the lack of the most elementary means of quantitative and qualitative chemical analysis limited all more thorough investigations of the nature of the changes in the components of the materials to more or less clever assumptions combination of assumptions, physical and chemical laws, and measured or sensory observation. Investigation of the origin of all visible changes, which could have been answered definitely and speedily with the proper chemical equipment, finally led to a construction of the various relationships which, while backed up by experimental findings, was still in many respects purely theoretical.

By its nature, an indirect approach to the crux of the problem required a lot of detail work. From the wealth of material available, we can highlight only those experiments which contributed considerably to the solution of the entire task.

If the change in the Frequenta of the first electrolytic soldering experiment is observed, it is noticeable that, in addition to the intensive blackening of the cathode contact area, the entire surface in the region of the covering by the sleeve has become discolored gray to black. The discoloration is more marked underneath the portions of the sleeve which touch the Frequenta than it is underneath the cavities where the sleeve does not touch the surface. However, even at those points, the surface may be nearly black, depending on the temperature and the strength of the current applied. On the anodic soldering point, with the exception of the brown contact area, and a few dimmer points where the sleeve directly touches the surface, the original color of the Frequenta has remained unchanged. (s Fig.5). The discoloring effect of negative electrodes which do not touch on opposite Frequenta surfaces was an interesting phenomenon. Determining its nature promised an valuable contribution to the understanding of the electrolytic soldering

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~~maximum temperature:~~

~~average electrolyte current: 20 ma.~~

~~Result of experiment: No visible change of color in the region of the Frequenta~~ FIRST EXPERIMENT ~~surface covered by the ring.~~

The experiment was carried out on newly made lead of 29 diam. of AS 42 with ~~the principle the same as in experiment 1a), except that there~~ A 71 ~~is an additional 3 mm hole in the ring, which is adjustable until it touches the~~ ~~edge of the sleeve below it. In that case, direct electrical connection with the~~ ~~soldering point was established.~~ an external graphite electrode. Before the second sleeve was pressed on, a ring ~~Circuit: Same as above~~ ~~Time of soldering at temperature above 1000°C: 60 minutes~~ ~~Maximum temperature: 1013°C~~ ~~average electrolyte current: 13 ma~~ ~~Result of experiment: Within the area covered by the ring, the surface of the~~ ~~Frequenta was colored gray, and a step-like unevenness of the interior wall of~~ ~~the Frequenta tube could be felt.~~ ~~Conclusion: Evaporation of silver at temperatures above 1000°C; 60 minutes~~ ~~and a small sheet-iron pocket, filled with silver, was welded to the outer~~ ~~circumference of the ring. Then only opening (a hole of 2 mm diameter) of this~~ ~~pocket ran through the ring to the surface of the Frequenta. The purpose of this~~ ~~arrangement was to direct a jet of vaporized silver onto the Frequenta. Graphite~~ ~~coating of the outer surfaces of the pocket was to speed the vaporization by~~ ~~increasing the heating of the pocket. During the soldering the ring was removed~~ ~~to a distance of about 3 mm from the edge of the sleeve underneath it by means~~ ~~of little ceramic washers and was kept in this suspended position; there was~~ ~~therefore no direct electrical connection with the soldering point.~~ of 25 mm, the position of the ring within the space could be changed.

Circuit: Both soldering points negative, auxiliary electrode positive.

Time of soldering at temperature above 1,000°C: 95 minutes

maximum temperature: 1038°C

average electrolyte current: 20 ma.

Result of experiment: No visible change of color in the region of the Frequenta surface covered by the ring.

b) Arrangement in principle the same as in experiment 1a), except that there is an additional 3 mm hole in the ring, which is adjustable until it touches the edge of the sleeve below it. In that case, direct electrical connection with the soldering point was established.

Circuit: Same as above

Time of soldering at temperature above 1000°C: 60 minutes

Maximum temperature: 1013°C

average electrolyte current: 13 ma

Result of experiment: Within the area covered by the ring, the surface of the Frequenta was colored gray, and a step-like unevenness of the interior wall of

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the ring are clearly represented (smaller distance: darker color). The grey color is interrupted by bright spots which are faint opposite the hole through which the silver vaper escaped, and which are clearly marked opposite the 3 mm hole.

e) Repeat of experiment 1b), but with one nickel and copper sheet each, ~~mounted~~ of rectangular shape, welded to the inner surface of thex ring. Average distance of the sheets from the Frequenta about 0.3 mm.

Circuit: Same as above

Time of soldering above 1000°C: 70 minutes

Maximum temperature: 1025°C

Average electrolyte current: 19 ma.

Result: All unevennesses shown in grey. The copper sheet stage is somewhat darker, the nickel sheet (stage) somewhat lighter than the surrounding surfaces.

Second experiment:

On a finished head of 20 diam. made of AS 42, both sleeves were connected by a metal loop at some distance from the Frequenta. Three iron electrodes of a diameter of 2 mm were attached to the loop in such a manner that their circular surfaces were directly opposite the free Frequenta surface without touching it. Electrode I was 3 mm away from the long sleeve. Electrode II was in the middle between the two sleeves and electrode III was 3 mm away from the short sleeve. The distances from the Frequenta surface, in the same order, were 0.25, 0.3, and 0.5 mm.

Circuit: Both soldering points and the bridge electrodes negative; internal electrode positive.

Time of soldering at temperature above 1000°C: 30 minutes

Maximum temperature: 1015°C

Average electrolyte current: 20 ma.

Result: Frequenta colored gray with grey circles of different intensity opposite the electrodes. Below electrode III the coloration is light grey, below ~~mm~~ electrode I medium grey, and below electrode II dark grey.

Third experiment:

A tube of AS 42 was mounted on an insulated stand made of ceramic tubes

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tubes. The tube had no sleeves, and was equipped with an internal electrode. The connection wire ran through the observation window, as usual. At half the height of the tube, a ring electrode was of 30 mm height and 21 mm internal diameter was placed eccentrically around the tube without touching it. The smallest distance from the Frequenta tube was 0.5 mm, the greatest 1.5 mm. The ring electrode was electrically connected with the housing of the vacuum furnace.

Circuit: Internal electrode positive, ring electrode negative.

Time of heating at 1025°C: 75 minutes

Transfer of current: 4 ma (start of a noticeable transfer of current at a temperature of approximately 800°C).

Result: The surface of the Frequenta was colored dark grey at the side where the tube and the ring electrode were adjacent together. Underneath the internal electrode, after it had been washed off, the Frequenta showed the brown color typical for the positive pole, but the coloration was slight, as corresponded to the low density.

Fourth experiment:

Two tubes of 12 ⌀2 of 22 mm diameter were provided with two 10 mm wide ring-shaped graphite electrodes, 2 mm apart from each other. Each electrode was connected to the DC leads by means of [illegible] wire. The tube was placed upright [illegible] on the iron base inside the vacuum furnace.

Circuit: lower graphite electrode negative, upper one positive

Heating time at an average temperature of 1025°C: 65 minutes

average electrolyte current: 9 ma

Result: Underneath the positive graphite electrode which has been washed off, the Frequenta was evenly colored dark brown, underneath the negative graphite electrode, the color changed from dark grey to black in the direction of the positive electrode.

A summarizing ~~Ka~~ summary of the results of these four experiments shows the following pictures:

The blackening of the cathodic surface of the Frequenta is the consequence of a change in the material of the ceramic electrolyte under the effect of the current generated by the electrical field applied to the electrolyte. The black or grey coloring opposite an electrode which is not touching, and the blackening underneath an electrode which is touching, are of the same origin. In the first

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case, the current transfer is accomplished by direct contact; in the second case by the emission of charge carriers. The question whether the emission of electrons by one material or the emission of ions by the other is the predominant phenomenon has not yet been settled. The qualitative cathodic conversion of material is independent of the type of current transfer, but quantitatively it depends on the current density. As a result, the electrode which does not touch is quantitatively dependent on the emission characteristics of the materials, on the gases remaining in the vacuum, and on the distance between the electrodes, and the potential drop. Experiment 2 is a very good illustration of this. If in this case, it is expected that the intensity of the blackening will be a function of the distance of the electrodes, then the actual result is contradictory. However, the relationship with the potential distribution in the Frequenta (Figures 7b to 7d) shows that the potential drop on the electrodes I and III is much less, because of the proximity of the sleeve, than it is on the middle electrode II. Therefore, the effect of the distance of the electrodes can be recognized in its pure form only on the two outer electrodes. The brown coloration underneath the positive electrode which touches also seems to be independent of the material of the electrode.

The following experiment was informative in regard to the kind of charge carriers which are emitted:

Fifth experiment:

The electrode material to be investigated - in the first case a Frequenta tube 70 x 20 x 16.5 of AS 42 - was placed on the iron base of the vacuum furnace, after the external sleeve and the lower front end had been coated with conductive graphite. A water-cooled double-walled iron electrode protruded into the upper portion of the Frequenta tube. The electrode was insulated by means of rubber rings, was fastened underneath the observation window, and was provided with tubes for the feed and removal of cooling water. The setup of the experiment is shown schematically in Figure 12. The setup was somewhat complicated, because the ground connection through the cooling water line had to be broken whenever a measurement was being carried out. This was accomplished by placing and insulated reserve vessel into the feed line, which took care of the water supply for a short time, while the flow was shut off. At the same time, the water flowed back into an insulated vessel in the return line. The upper portion of Figure 12

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shows the cooling water lines inside the head of the electrode. This setup permitted the measurement of the emission of charge carriers due to thermic effects.

The measuring of the emissions on the Frequenta could be carried out only up to a temperature of 960°C , because of the high radiation losses in the direction of the cold electrode. However, it is obvious from the measuring points in Figure 13, that the electron and ion currents flowing at a temperature of 960°C and an anode potential of 105 v are of the same order of magnitude. The same measurements, performed on an iron tube of the same interior diameter showed very similar results (Figure 14).

In addition to the emission measurements, the current transfer and the behavior of the Frequenta surface, when it was not touched by the positive electrode, were investigated.

Sixth experiment:

The setup of the experiment was the same as in the third experiment.

Circuit: Positive ring electrode, negative internal electrode.

Time of heating at temperature of 1035°C: 70 minutes.

Current transfer : 3 to 4 ma at 400 v.

Result: Even at a very small distance of the electrode from the surface, no visible discoloration of the Frequenta occurred. The entire area underneath the internal electrode which had been washed off was colored light grey.

The results of these six experiments give no indications on the ion ions themselves. However, enough material can be compiled from these results to arrive at intermediate conclusions. It is known that some metal ions of the Frequenta will move in the direction of the cathode, if an electric field is set up by two electrodes separated from each other by the ceramic electrolyte. On the contact surface, these ions will effect a black coloration, and favor the adsorption of silver atoms (Figure 15a). It is also known that negative ions will migrate to the anode, taking along oxygen which is released there and colors the contact area brown.

The results of the experiments can enlarge the knowledge of the electrolytic process by some of the conclusions. If, for instance, the situation with the negative electrode not touching the surface is considered, as shown in Figure 15b, then experiments 1 to 3 will indicate that the electrolytic process is taking place here less intensively, but nevertheless in otherwise unchanged form.

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Experiment 5 shows that it is absolutely possible that a bipolar exchange of charges takes place on the cathode which does not touch the surface, at soldering temperatures; both positive Frequenta ions and electrons of the iron electrode can serve as a bridge for the current across a narrow gap. Extrapolation of the emission measurements and the minimum temperature for incipient current transfer as indicated in experiment 3 make the proportion of the positive charge carriers in the total current seem small as compared to the proportion of the electron emissions, and in fact may be ~~provided the positive charges are not~~ altogether negligible. The true state of affairs is probably one in which the cations transported to the surface of the Frequenta from the lower layers are neutralized there by the impinging electrons.

The situation is different when the electrode which does not touch the surface is positive (Figure 15c). The current transfer in this case is much less and the blackening of the cathodic contact area is correspondingly slight. It is particularly striking that there is no brown coloration on the surface opposite the anode. As migration of ions is connected with the transport of matter, and as the discolorations of the Frequenta are a consequence of these changes in matter, it must be assumed that the migration of ions takes place only in one direction when the anode does not touch the surface. The cation transfer number then will equal 1. There are two explanations for the fact that an electrically neutral condition is maintained despite this. One explanation is based on the assumption that the iron ions leaving the anode because of thermo-ionization (experiment 5) find good electrolytic means of movement after impinging on the Frequenta surface and thus migrate to the cathode. The correctness of this explanation could be checked by using various types of anode materials, e.g. graphite. A second explanation considers the release of electrons by the Frequenta due to thermal effects (experiment 5) as dissociation of neutral metal atoms into cations and electrons. The electrons go to the anode, while the metal ions will migrate in the opposite direction, to the cathode. There they are neutralized by taking on an equal negative charge.

After the first experiments had established a sound basis for the future detailed work, the main interest was directed toward determining the nature of the ions. Some of the most important findings along this line will be shortly

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described below. At first, however, a supplementary explanation must be given:

The representation of the electrolytical phenomena until now described the visible changes in the Frequenta, as they occurred during the first soldering experiments. It turned out, however, in the course of time, that, in addition to the brown anode layer and the black cathode layer, a light brown layer may appear underneath the cathodic Frequenta contact surface. This light brown layer, to be called brown cathode layer (Figure 1b) to distinguish it from the brown anode layer and the black cathode layer, is located between the black layer and the interior of the Frequenta material, and cannot be detected easily from the outside. Its max thickness depends to a great extent on the iron oxide content of the Frequenta and on the density of the current applied. In the first experiments which were carried with AS 42 which had a low oxide content, this layer was detected only at above-average current densities. With the AS 42 C material which was used most of the time later on, a very maximum definite layer of this kind appeared already at average current densities. The reasons for its occurrence have not yet been satisfactorily established, but it can be assumed from the observations which are available that it is formed by the same kind of negative ions which causes the brown coloration of the anode layer. For the time being, the explanation advanced for the peculiar position of the brown cathode layer states that the anions move much faster within away from the cathode within the black layer than they can move from the inner border of the black layer through the rest of the electrolyte. This explanation, thus, would attribute the brown coloration to the accumulation of anions.

Seventh experiment:

The black Frequenta layer adhering to the silver surface of a soldering test piece which had been opened was carefully removed from the silver, cleaned of iron particles with a magnet, and all traces of silver or iron not bound to the ceramic were removed by means of acid. The material was then treated with hydrofluoric acid and a rough qualitative analysis was carried out to determine the presence of iron and silver.

Result: Precipitation definitely showed a considerable iron content. A slight trace of silver was considered to be not impossible, but unlikely.

Eighth experiment:

The dark-brown anodic contact surface of a Frequenta tube made of AS 42 was

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dissolved in hydrofluoric acid and the sample was tested as above.

Result: Iron content could be established with certainty. The presence of silver could not be determined.

Ninth experiment:

The Frequenta tube of an electrolytically soldered lead of 29 mm diam., made of AS 42, without the brown cathode layer, was freed of the sleeves and the internal electrode, and heated at 1025°C in the vacuum furnace for one hour.

Result: The cathode layer, previously deep black, was slightly lighter, the grey layer created by emission had disappeared completely in parts, the previously brown anode layer had turned iron-grey.

Tenth experiment:

Same as above, except that a Frequenta tube of AS 42 C with a strong brown cathode layer was used.

Result: The previously deep-black cathode layer had turned medium grey, the previously brown cathode layer (as far as it was visible) had completely turned back to the original color of the Frequenta. The previously dark-brown anode layer had turned dark iron-grey.

Eleventh experiment:

The Frequenta tube of an electrolytically soldered lead of 29 mm diam., made of AS 42 C with strong brown cathode layer was freed of sleeves and internal electrode, and heated to 600 to 700° C for several hours with access of air.

Result: The previously deep black cathode layer had turned dark brown on the surface, the previously grey layers had become light to medium brown in color. The brown cathode layer (as far as it was visible) had not changed. The previously dark brown anode layer had turned a deep rust color.

Twelfth experiment:

A group of pencil marks, 3 mm in length, and another group, 12 mm in length, were made in a longitudinal direction on the free ceramic surface of a soldered lead of 29 mm diam., made of AS 42. The lead was then again soldered electrolytically.

Circuit: As shown in Figure 8a, but without the auxiliary electrode.

Time of soldering at temperature above 1000°C: 125 minutes

Maximum temperature: 1055°C

Average electrolyte current: 4.5 ma

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Result: Each pencil mark (graphite), after it had been sealed off, was shown on the surface by a black and brown discoloration. Independent of the position between the sleeves and of the length of the mark, a constant length ratio of 1:5.25 between the black and the brown part was noted.

Thirteenth experiment:

Same as experiment 12, except with only one group of pencil marks of an average length of 4.5 mm. Soldering with auxiliary electrode.

Circuit: Both soldering points negative, auxiliary electrode positive.

Time of soldering between temperatures of 900 and 1010°C: 22 minutes.

Maximum temperature: 1010°C.

Average electrolytic current: 15 ma.

Result: Again black-and-brown markings made by the graphite lines. However, the length ratio of the colors varied according to the position toward the sleeves between 1 : 1.6 and 1 : 0.5.

Fourteenth experiment:

The electrolytically discolored Frequenta of experiment 4 was marked in such a manner with narrow graphite rings that two rings each were 0.6 to 0.7 mm apart from each other on the uncolored, the brown, and the black portions of the surface. The resistance of the three types of surfaces was measured by means of a mirror galvanometer ($I^0 = 3 \times 10^{-9}$ a) and 400 v DC. According to the test specification, the electrodes are to be 10 cm long, knife-shaped, and set 1 cm apart; the air humidity is to be 80%. In this case, the air humidity was not taken into account, and the resistance values obtained can therefore be compared only with each other. The surface resistance, determined from ten measurements and converted to the values of the specified electrodes was

For the not discolored surface	0.4×10^9 ohm
for the brown surface	0.93×10^9 ohm
for the black surface	1.14×10^9 ohm.

According to DIN 40615 specifications, the surface resistance of standard Frequenta is between 10^9 and 10^{12} ohm.

These above experiments represent only a small, but characteristic portion of the experiments performed. On the basis established by these experiments, it was possible to analyze the electrolytic process in some of its important aspects,

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Result: Each pencil mark (graphite), after it had been wiped off, was shown on the surface by a black and brown discoloration. Independent of the position between the sleeves and of the length of the mark, a constant length ratio of 1:5.25 between the black and the brown part was noted.

Thirteenth experiment:

Same as experiment 12, except with only one group of pencil marks of an average length of 4.5 mm. Soldering with auxiliary electrode.

Circuit: Both soldering points negative, auxiliary electrode positive.

Time of soldering between temperatures of 900 and 1010°C: 20 minutes.

Maximum temperature: 1010°C.

Average electrolyte current: 15 ma.

Result: Again black-and-brown markings made by the graphite lines. However, the length ratio of the colors varied according to the position toward the sleeves between 1 : 1.6 and 1 : 0.5.

Fourteenth experiment:

The electrolytically discolored Frequenta of experiment 4 was marked in such a manner with narrow graphite rings that two rings each were 0.6 to 0.7 mm apart from each other on the uncolored, the brown, and the black portions of the surface. The resistance of the three types of surfaces was measured by means of a mirror galvanometer ($1^{o} = 3 \times 10^{-9}$ a) and 400 v DC. According to the test specification, the electrodes are to be 10 cm long, knife-shaped, and set 1 cm apart; the air humidity is to be 80%. In this case, the air humidity was not taken into account, and the resistance values obtained can therefore be compared only with each other. The surface resistance, determined from ten measurements and converted to the values of the specified electrodes was

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A few findings to connect these data are missing, and a complete overall picture could therefore not be evolved. These data could have been established only by exact chemical methods in order to be indisputable. Staining by layers and analysis of a Frequenta surface discolored by a very little electrode, or spectroanalysis of the colored layers would certainly have been very informative. These investigations could not be carried out because the necessary apparatus and auxiliary equipment were not available. It was therefore necessary to establish a logical connection between the observations which depended mainly on the methods employed by the individual researchers and on their good judgment.

The final findings are based on an assumption which has not yet been proved, namely, that the conductivity of the Frequenta at the temperatures in question is due to the ions of the dissociated Fe_2O_3. The assumption is supported by the fact that the resistance is especially high as compared to most other ceramic materials. This can be attributed to the lack of alkali ions and also to the dependence of the resistance on the Fe_2O_3 content, observed in the experiments and confirmed by Stomag.

The conductivity of the solid electrolyte, which increases continuously at higher temperatures, shows that ions must be present already at an early stage, but that their mobility is very small. In that case, the ions are still fixed in the space lattice, i.e., their oscillations are still so slight that they will not arrange themselves in a definite direction under the influence of an external force (the electric field). The oscillations increase only at higher temperatures, and in connection with a higher degree of dissociation cause the conductivity to increase. The oscillation, caused by the taking up of thermal energy, then reaches the point where the ideal lattice arrangement is disturbed. Atoms, or groups of atoms, which can again appear in the form of complex ions or molecules, will leave their places in the lattice and will then occupy places between the lattice, or, if several atoms exchange places, they will be in the wrong place in the lattice. This formation of holes is of great importance for all processes of motion in the crystal, such as diffusion and conductivity. It also explains how these Fe_2O_3 ions can move through the lattice of the solid electrolyte under the influence of electrical directive forces.

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It is quite possible that the degree of hole formation of the components of the silicate crystals -hich consists of a number of very dissimilar kinds of atoms, is very unequal. The Fe_2O_3 ions, as electrically weakly bound [illegible] structural elements may show strong hole formation while the other more strongly bound structural elements still remain undisturbed. The cation and anion lattices of the Fe_2O_3 can be imagined to be already in the molten state at soldering temperature. In that state it will fill the spaces of the rest of the lattice, while still bound by the ionic forces within the electrolyte without a field, like water fills the pores of a sponge.

If the observed phenomena are to be brought into an orderly relationship, the Fe_2O_3 (provided it is really the exclusive carrier of the conductivity) would have to be dissociated into one Fe cation and one O anion. The occurrence of a pure O anion is in itself improbable, and furthermore, it was shown by the experiments 9 to 11 that the brown anode layer definitely contains such a high proportion of iron that it cannot be explained by the normal Fe_2O_3 content of the Frequenta, as [illegible] might have been possible in the case of experiment 8. These annealing tests also have convinced the researchers that the anion must be a complex ion formed of Fe and O. This led to the theory of the electrolytic process shown in Figure 16 in schematic form. According to this, the neutral iron oxide dissociates into a trivalent cation and a trivalent complex anion:

$$Fe_2^{+++}O_3^{--} \rightarrow Fe^{+++} + (FeO_3)^{---}$$

It is known of the anion that it liberates oxygen at the anode. This can happen in two ways:

1.) $2(FeO_3) \rightarrow Fe_2O_3 + O_3\uparrow$

2.) $(FeO_3) \rightarrow FeO + O_2\uparrow$

Case 1 is very unlikely to occur, because the concentration of Fe_2O_3 remaining on the surface of the Frequenta is saturated -ith oxygen and could not change its color any more when annealed with access of air (experiment 11). In case 2 theory and test results coincide well. An iron-oxygen concentration of the lowest stage of oxidation will be formed on the surface, and when annealed in air (Figure 17), it will turn into reddish-brown iron oxide, thus:

$$2(FeO) + O \rightarrow Fe_2O_3 .$$

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During the soldering, a reaction between the liberated oxygen and the carbon to form carbon dioxide can be expected on the positive graphite electrode.

The trivalent iron cation migrates to the silver electrode, and becomes a neutral iron atom by the compensation of the triple negative charge given off at the anode. Stronger concentration of iron atoms leads to grey or black coloration of the Frequenta surface. The proof of a higher percentage of iron in experiment 7 is no definite proof of this statement, but it is further strengthened by the result of experiment 11. According to this, the external boundary layer of the blackened area becomes brown iron oxide (believed to be this compound by its appearance)

$$2\ Fe + O_3 \rightarrow Fe_2O_3. \qquad \text{(Figure 17)}.$$

The brown cathode layer whose occurrence was explained by the accumulation of the anions originating in the black layer can also be explained, while maintaining the assumption of different ion velocities, by the theory that the much slower anions are forcibly displaced from the vicinity of the cathode by the faster cations, until they can migrate without interference from the accumulated layer with their own natural velocity.

According to the theory, the brown cathode layer consists of an accumulation of complex anions. In annealing in air of the exposed layer, no change in color should take place, as the compound is already oversaturated with oxygen and the temperature is not high enough for compensating labile constellations of matter. This was confirmed by experiment 11. Experiment 10 shows very well that the formation of layers near the cathode effected by the influence of electrical forces is a forced disturbance of the equilibrium. After annealing in a vacuum at 1025°C the black layer has nearly completely turned back to the original color of the Frequenta, while the brown cathode layer has completely returned to the original color. Obviously, the equilibrium has been reestablished here by an exchange of both types of ions.

The fairly detailed report on experiments 12 and 13 was not given to provide a concluding interpretation, which can be given only to a limited extent at the present time, but as a supplement to the investigations of electrolysis of Frequenta and as a guidepost for further work along those lines.

If a short conductor is placed on the free Frequenta surface of a lead which is to be soldered electrolytically, with this conductor (e.g. a pencil mark of

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graphite) not connected to the electrodes, and running in the direction of the lines of flux, then the flux lines in the vicinity, attracted by the path of least resistance, will run through this conductor and turn it into a dipole. If sufficient amounts of electricity flow, the Frequenta will be colored brown and black in a definite length ratio along the line of contact with the dipole. As far as the soldering process is concerned, this phenomenon at first seems to be irrelevant, but it can be proved that the ratio of length of the lines of different color is related to the processes taking place in the electrolyte and can supply important data for determining the nature of the ions, if properly evaluated.

Before we investigate the regularity of the length ratios more closely, we shall first describe the path of the electric current through a "line sonde" (pencil mark) with the help of the sketch in Figure [illegible]. The [illegible] have been marked in a simplified manner as Fe^{+} and O^{-}. The lower portion of the sketch shows a longitudinal section through the wall of a Frequenta tube with a silver electrode. Above this, a schematic top view of the same electrode with the two groups of "line sondes" (experiment 12) is shown, with one "sonde" picked out and represented as projected onto the surface of the Frequenta. If we start with the simplified assumption that only primary electrolytic conversions with the generation of free atoms take place under the influence of the electric field, then the flow of current can be explained as follows: The potential difference of the line sonde and the silver electrode is determined by a potential area which touches the polar reversal point of the sonde. The total potential between the electrodes is thus subdivided along a short portion of the flux lines into two sections (in the figure e.g. 30 and 70 % of the total voltage), each of which has the same electrolytic characteristics as the total section, i.e. the cations move toward the right, and the anions toward the left. The Fe^{+} ions discharging on the cathode are neutralized by the electrons of the external circuit, while the O^{-} ions, migrating in the opposite direction, will give off the same quantity of electrons to the sonde. The influx of these electrons into the right part of the sonde enables the left part to give off the same amount to the Fe^{+} ions arriving from the direction of the anode. An analogous process takes place from here to the anode and closes the internal circuit.

The total area of contact of the sonde is divided by the two types of ions

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into a certain proportion which, if the width of the lines is constant, can be expressed by the length ratios. If F_k is the partial area, along which the cations are neutralized and if F_a is the partial area along which the anions give off their charge, then the quantity Q of electricity transported here through each of the partial areas per unit of time is a product of the valence z, the mean velocity w and the density c of the ions.

$$Q = w \cdot z \cdot c \cdot F$$

As the quantity of electricity which arrives must be equal to the quantity of electricity which flows off,

$$Q_k = Q_a$$

or

$$w_k \, z_k \, c_k \, F_k = w_a \, z_a \, c_a \, F_a .$$

Thus we obtain an area ratio

$$F_a / F_k = (w_k \, z_k \, c_k) / (w_a \, z_a \, c_a)$$

According to the theory of the electrolytic process (Figure 16), both ions have the same valence, and there is some justification for the assumption that the number of ions within one unit of space will be the same. Thus we obtain the simplification

$$F_a / F_k = w_k / w_a = K \text{ (Material constant)}.$$

The partial lengths of a sonde are thus inversely proportional to the mean velocities of the ions in them. If the temperature always remains the same, and if w_k / w_a is measured along the parallel bundle of flux lines, it is a material constant of the Frequenta mass, and has been determined as 5.25 for AS 42 at 1025°C (Experiment 12, Figure 16). By means of this constant, the dispersion of a bundle of flux lines can be roughly determined at any point on the surface of the Frequenta. Figure 19 ([illegible]) shows as example, how a group of line sondes can be used to measure and to make visible the change in density of the flux lines. If K is known, and if D_a is the density of the flux lines underneath the brown end of the line sonde, and D_k the density underneath the black end, the formula for the standard circuit (both soldering points negative, auxiliary electrode positive) will be

$$D_a / D_k = F_k / K F_a$$

and for the reversed circuit (both soldering points positive, auxiliary electrode negative) it will be

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$$n_a/n_k = v_k / v_a$$

The change of density of strongly dispersed flux lines is best determined by means of short line anodes, but even then the requirements for great ion must not be set too high, because the distance within which the change in density is to be determined cannot be defined exactly because of the finite longitudinal extension of the two sections of the anode. The determination of the constant F over the parallel bundle of narrow flux lines, however, can be determined very accurately. For example, the average values from the two line anode groups in Figure 18 (Experiment 12) checked perfectly.

The quantity of electricity transported by each kind of ions is proportional to the velocity of these ions. In the example cited for the constant K_{18}/K_2F is 5.25, i.e. the velocity of the cations is 5.25 times that of the anions. If the figures are made into whole numbers, it can be stated that an assumed passage of 25 current equivalents will be distributed over both types of ions at the ratio of 4 : 21. If these relative values are substituted for the ion velocities, we obtain for the portion of the total quantity of current, which is transported by the cations

$$n_+ = v_k / (v_k + v_a) = 21 / (21+4) = 0.84$$

and for the portion transported by the anions

$$n_- = v_a / (v_k + v_a) = 4 / (21+4) = 0.16$$

In the assumed passage of 25 current equivalents there will be a loss of 21 at the anode, and a loss of 4 equivalents of electrolyte at the cathode. This statement confirms the theory on the generation of the brown cathode layer: The anions are crowded out by quick influx of cations, but due to their low velocity they can migrate only slowly through the ~~the~~ electrolyte and accumulate at the interior boundary of the black layer.

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D. The DC Apparatus

Soon after the first electrolytic solderings had been carried out, employing dry-cell batteries as DC source, a mains-operated set which fulfilled the special requirements was developed. The set supplies a maximum of 400 v DC and uses a current of 200 ma. The ripple is approximately 2%. The wiring diagram is shown in Figure 20, the external view of the set with the front panel for the switches and controls is shown in Figure 21.

The device operates as a double-wave rectifier with two RG 11 tubes with their plates in parallel. In order to allow easy controlling of the DC voltage, the tubes are permanently heated through a small heating transformer of 220/ 4 v after the line voltage has been turned on, while the plate AC voltage of 2 x 400 v is supplied by another transformer whose primary voltage can be varied between 0 and 220 v through a potentiometer.

A filter network of two electrolytic condensers of 8 µf/ 450 v and a choke of 200 ma/ 6 henry serve for smoothing of the voltage. The voltage indication is accomplished by a rotary-coil voltmeter of 0-5000 v, the current indication is carried out by a shunted milliammeter with a measuring range of 0 - 200 ma, and 0 - 100 ma if the key is depressed.

The set also contains single-pole switches for turning on the line voltage and the DC, and a 1 amp fuse for the line side and a 0.2 amp fuse for the DC side. A switch coupled with the potentiometer permits the shutting off of the latter while no measurements are being taken, without necessitating interruption of the heating for the tubes. Because of the operating voltage of the electrolytic condensers the DC circuit must not be shut off without lowering the DC by means of the potentiometer. The DC, which in no-load condition rises to as high as 550 V, would otherwise cause the condensers to break down.

E. Soldering Holders and Racks

The special requirements of electrolytic soldering have led to the development of soldering holders which, containing a number of equal leads, are inserted into the soldering furnace. Figure 22 shows one holder each for the lead sizes 16, 29, and 52 mm diameter. The holder consists of a base plate with the top holder supported by columns which are made of perforated sheet iron (for 16 mm) or of attached strips of sheet iron(for 29 and 52 mm diameter). The base plate

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tubes. The greatest diameter of the device depends on the space available within the quartz cylinder inside the vacuum furnace. In our case, this is about 140 mm. This size is sufficient for

12 leads of 16 mm diameter

10 leads of 20 mm diameter

4 leads of 32 mm diameter

1 lead of 60 mm diameter.

Only leads of the same size can be soldered simultaneously. Layer plated into the holder lead downward, and the lead sleeves are connected with a thin iron wire in such a way, that the wire is looped around each sleeve. The end of the wire is connected to the holder. The touching of the base plate by the head of the lead under the force of gravity affords sufficient electrical contact. Then the movable plugs or inserted and the contact pins are connected with each other by means of a thin iron wire. This can be done by simple looping of the wire or by attaching iron clamps fastened to the wire.

Figure 22 is taken from the previous report No 221, when the connection between the auxiliary electrodes and the insulated positive current lead still was carried out over a contact plate supported by the contact pins. In the meantime, the contact plate has become superfluous. The new type of current supply runs through a so-called soldering rack which is permanently set up in the furnace (Fig.23). The rack combines the iron base, on which the holder and the quartz cylinder are set, with a contact star of sheet-iron supported on three long ceramic columns.

The soldering racks are installed in the following manner: The contact star, resting loosely on the columns, is removed; then rack and quartz cylinder are placed on the base, and the contact star is put back on. Finally, the end of the iron wire which connects the auxiliary electrodes is wound around a protrusion on the contact star, which is provided for this purpose. The loss currents for the columns which are no longer fully insulated at soldering temperature is at the most 4 ma in this case.

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F. The Insulated Line into the Vacuum Furnace

The vacuum furnace is equipped with an additional insulated current lead for electrolytic soldering (Fig. 24). An iron ring is held between rubber washers underneath the observation window in the center of the furnace cover in such a manner that a contact-tube lead, connected to it by three bridges, protrudes into the vacuum vessel, insulated from it. The contact tube can easily be moved in an axial direction. Its movement in a downward direction is limited by a stop pin. The connection with the contact star of the soldering rack is carried out by having the lower end of the contact tube touch the contact star when the cover of the furnace is lowered, so that it will be pushed upward slightly on contact (Fig. 24). The weight of the contact tube produces the required contact pressure. During the soldering, the temperature measurement point in the soldering rack can be sighted through the contact tube and a centered hole in the contact star.

G. The Electrolytic Soldering Process

The entire vacuum-soldering process, starting with the evacuation of the furnace after the items to be soldered have been placed into it, and ending with the letting in of gas after the soldering process has been finished, is the same in all details as the one described in reports Hg 102b and Hg 119. The electrolytic effect on the soldering points is carried out within this process by means of the special equipment described, and according to the following directions:

Prior to the evacuation of the closed furnace vessel, the interior DC line is tested between the vessel and the insulated lead on the observation window, to determine if it carries current. If the arrangement has been properly set up, no current should flow. Only after this test has been carried out, evacuation is performed, the coolant tank is filled, and the furnace heating is turned on according to the method prescribed, depending on the type of lead being soldered. The DC is turned on only when the temperature of the leads is approaching 2000 C. From this point on, the electrolytic treatment is carried out according to definite rules which have turned out to be practical in the course of the development of the method.

The strength of the electrolyte in the Frequenta is proportional to the duration of the electrolysis, if the current density remains the same. If the current is constant, and the electrode area is known, the time is a direct

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measure for controlling the electrolytic process. However, since the ionic conductivity is constantly changing during the time of action of the DC, the current does not remain at the level for which it has been set originally; it is kept approximately constant by regulating the voltage. The most favorable range of current density as worked out during the time of development is between 1 and 2 ma per sq. cm. for AS 42, and between 1 and 1.5 ma per sq. cm for AS 42 C. It should be noted that the current density has been calculated from the total current and the average silver surface in contact, but that in reality a partial current which cannot be measured flows directly above the contact points, and as emission current between the sleeve and the Frequenta. Lower current densities require longer soldering times, for the same effect; current densities above 2 ma per sq. cm can cause burning of the Frequenta surface even at normal soldering temperatures. The sensitivity to current overload increases with increasing ZrO_2 content of the Frequenta. Local current overloads can occur on accidental points of contact of the silver strip, if the full electrolytic current is used at temperatures below 960° C. It has thus been found to be of advantage to carry out the de-oxidation of the soldering point at a temperature between 900 and 1000° C, i.e., while heating to the soldering temperature is still in progress, with only a portion of the maximum current (about 20% of it). The maximum current is determined for every lead size by the product of the permissible current density and the electrode surface. Some restrictions, however, are required also in this case, because the maximum current cannot be reached in every case with the 400 v available, depending on the type of Frequenta and the diameter. In the case of the smallest leads (16 mm diameter) another difficulty arises. Due to the closeness of the electrodes the sensitive fuses tend to burn out already way below 400 v, and the leads break down, while their small internal diameter causes an unfavorable ratio between negative and positive contact areas, according to experiences with line sondes about 1 : 5.25. Considering these circumstances, the following practically applicable current values have been established, which remain turned on for 60 minutes, independent of the original partial current, and which will have the desired electrolytic effect at the average soldering temperature of 1025°C:

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For 16 mm diameter leads of AS 42: 6 mm

For 29 mm " " " " " : 20 mm

For 29 mm " " " AS 42 G : 15 mm

For 52 mm " " " " " : 50 mm

For 60 mm " " " AS 42 : 30 mm.

Starting at a temperature of approximately 900°C, the electrolytic process takes place according to the characteristic shown in Figures 25 to 27. The diagrams show that 20% of the permissible current is turned on during the heating to soldering temperature, and that the maximum current is turned on when 1000°C has been exceeded. The resistance characteristics of the lead, which are shown in, show, in addition to the general dependence on temperature, that the current - and voltage sensitivities increase as time progresses. This might be attributed to the progressive electrolytic conversion which raises the resistance. This would also explain the fact that the current itself must be regulated every now and then, after the soldering temperature has been reached.

At the end of the soldering process, the vessel is filled with nitrogen, as usual, and the heating current is shut off. The following points must be remembered in this case:

The effect of the electrolysis, which deoxidizes and causes regrowing of the material and thereby better binding, must not be interrupted, as long as noticeable regenerations can take place in the Frequenta due to the effect of temperature. This danger is practically eliminated at natural cooling temperatures already below the solidification temperature of the silver. It is necessary, however, to reduce the DC prior to the increase of pressure (admitting of gas) to a value which lies below the ignition voltage of glow discharges. At voltages below 100 v this is ensured. Thus the DC during the admitting of the gas can be only a part of the maximum current. After the gas has been admitted, higher voltage and thus also higher current can be used. The benefit from derived from this renewed increase, however, is slight, because the resistance of the Frequenta increases quickly after the heating has been shut off, and will cause the DC to decrease just as quickly at a given voltage. It is therefore more advantageous, for the purpose of better control of the amount of electricity supplied, to set a partial current and to keep it constant, similar to the method used with the initial current between 900 and 1000° C (Figures 25 to 27).

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After the DC has been shut off at approximately 2000 C, the electrolytic process is finished. The further treatment of the leads is carried out according to the directives given in report Fg 110.

It should be mentioned as a supplementary information, that in nearly all cases a peculiarity has been observed. According to theoretical considerations, a sudden decrease of the resistance should occur at the moment of the melting of the silver, at 960° C, because the contact between solder and fragments has been improved. In practice, however, the resistance curve shows only a very slight decrease at that point, and that only in very rare cases. This is to be attributed to the fact that a large portion of the current is transmitted as charge-carrier emission prior to the melting of the silver. This current can take the place of the contact current across the silver electrode, which sets in later. The blackening of the fragments within the sleeve outline which contain no silver, is generally so intense, that it cannot have occured during the short period of effectiveness prior to the melting of the silver. It must rather be assumed that part of the current is exchanged by emission between sleeve and fragments during the entire soldering process, in addition to the transmission across the liquid silver electrode.

The correctness of the above theory was proved by measurements carried out on two specially built leads which contained no silver. During the first measurement, the lead was subjected to the same temperature as in soldering, and the resistance was determined from time to time at voltages of 20, 100, and 150 V from the amount of current passing through. When recorded in the diagrams shown in Figure 23, to their relative positions, they showed a similar dependence of the resistance on the voltage, as had been observed in the soldering diagrams. In addition, the resistance as a function of temperature, and its values were at soldering temperature, one no similar to the diagrams obtained during soldering with silver, that it can be concluded from this that the silver contact has only a slight effect on the total transmission of current between sleeve and fragments. The discontinuity in the resistance curve at the end of the diagram in Figure 23 is caused not by the voltage sensitivity of the resistance, because the voltage remains constant for each diagram, but is due to the stopping of the emission current shortly after the pressure has begun to increase (admitting of gas).

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The second measurement carried out on a lead without silver was carried out, as far as the electrolytic treatment is concerned, along the lines of a silver solder job of the same diameter. Here, too, the slight influence of the silver contact on the total resistance was confirmed (Figure 29). The diagram shows the same characteristics up to the point of admission of the gas, and thereafter nearly the same resistance as occurs in normal solderings. A deviation occurred only in the last part of the measurement. The increase in resistance, marked by "a" in the diagram, is caused by reduction of current and voltage, and the admission of gas, which in the diagram coincides because of the slight time difference. When the DC was raised again to the normal value after the admission of gas had been finished, the resistance dropped again by the value a - b. This shows that the change b of resistance is due to the cutting off of the emission current, and a - b is due to a change in voltage. The measurement also proved that the contact losses of badly fitted electrodes are completely made up for by the emission current.

11. Concluding Remarks

The experiments started in October 1947 have brought such definite results in a very short time, that the entire production of leads could be converted to the electrolytic method by January 1948. This fact alone is a proof that the method is thoroughly understood and feasible.

The new soldering method has not only allowed the production of flawless soldering jobs with Frequenta AS 42 C, but has also made it possible to use the stocks of AS 42 which are still available with a minimum of rejects. Superficially, there seems to be hardly any difference between the two solder connections, but detailed tests show the connection employing the material which contains more oxygen to be better. It is therefore planned to use AS 42 C exclusively in the near future.

Figure 30 shows a good electrolytic solder connection between silver and Frequenta AS 42 C. A solid black ceramic layer, attached to the thinner portions like enamel, and a sputter- and bubble-free silver surface, which shows clearly the impressions of the irregularities and pores of the Frequenta surface, are the typical marks of this solder connection which is hardly in need of any improvement.

Statistical data on the amount of rejects in hard-soldered leads give a true picture only when the survey has been made on the basis of a large number of

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items. Of the 204 leads which were electrolytically soldered between January and September 1948, 166 were of the most common size, 29 mm diameter. The statistical evaluation of these 332 individual soldering points showed a rate of rejects of 7%. Of the same number of leads of same diameter, not soldered by the electrolytic method, during 1947, 16% had to be rejected. The rate of rejects has thus been reduced by more than half since the introduction of the electrolytic method. This success should be considered of even greater importance, because the possibility of reducing the rate of reject becomes greater as this rate goes down.

The greater part of the rejects, (about 4% of the total number of leads manufactured), is due to the better soldering characteristics of the Frequenta. This sounds paradoxical, but it makes sense, if it is recalled that the main reason for these rejects, upon their investigation, turns out to be one which did not occur very often prior to the introduction of the electrolytic soldering process. The cause is the appearance of flaws in the silver, which frequently leave the upper ring edge of the soldering zone completely filled, or interrupt the ring all along its width (Figure 31). Obviously, the force of the surface tension which is supposed to press the liquid silver into the soldering zone, is no longer sufficiently great.

Figure 32 shows the effective forces of the surface tension. Superficially, the only difference between normal and electrolytic soldering seems to be in the angle of contact between the silver and Frequenta surface. In normal soldering this angle φ is greater than 90°, and the silver does not wet, while it is less than 90° in the electrolytic soldering, and the silver will wet. The vertical components of the forces at the points C and D are equal and opposite in both cases, and cancel each other. The vertical components of the forces in the points A and B are directed upward in both cases; they add and attempt to move the silver upward. Thus only the forces on the wall of the sleeve can cause a change in location, and the magnitude of the force acting upon the silver is the same in both cases. However, if we consider the forces which attempt to prevent the silver from moving upward, we find them to be mainly the weight of the liquid silver column and its friction along the walls of the soldering gap. The weight of the silver column is the same in both cases, the friction along the iron surface is also the same, but the friction along the Frequenta surface is determined by the degree of wetting, which, in turn, is the same as the soldering quality.

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An angle of contact less than 90° means that the resultant of adhesion and cohesion is directed toward the Frequenta. The silver is attracted more strongly and the friction will increase (schematically indicated in Figure 42 by the forces R_1 and R_2).

Of the two vertical forces acting upon the silver, the force acting at point B is the predominant one, as long as the liquid metal hangs down below the coated area in sufficient quantity. The angle of contact, in this case, can be taken as 180°. The force along the entire circumference of a sleeve of a diameter of the soldering space of 90 mm (diameter of the lead: 20 mm), acting with at point B is then 8.8 grams (surface tension silver against vacuum assumed at 920 dynes per cm). Together with the force attaching at point A, which can only be estimated, the sum of the forces acting on the silver ring and directed upward can be assumed to be 10 to 12 grams. Of this, over 5 grams will be used up for compensating for the weight of the silver, and the force required to overcome friction must be deducted from the remainder. Only what is left after that is used to generate the pressure which forces the silver into the soldering zone.

It is thus evident that increase of the soldering qualities of the Frequenta are at the expense of the soldering pressure. It is possible to get around this difficulty by seeing to it that the soldering zone is at the lowest point within the soldering space. In this case, the forces of the surface tension will act in the direction of the force of gravity, i.e., they are supported by the weight of the silver. Proper redesigning of the sleeve can still maintain the membrane effect of the sleeve wall on both sides of the soldering zone. Continuation of the development indicated here is a worthwhile task, and would serve to reduce the rate of rejects by another 4%.

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APPENDIX

Testing of dielectric strength of ten electrolytically soldered leads of 29 mm diameter, before and after temperature and vacuum test

(Testing with continuously increasing AC voltage)

No. of item	Cracking at kvolt before	after
29/347	17.9	18.7
29/359	17.9	20.7
29/360	17.9	19
29/362	18	21
29/369	18	21
29/[illegible]4	17.9	19.9
29/386	18.5	19
29/389	17.9	19
29/405	24	29
29/412	18	19.2

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Figure 1.

Bezeichnung der Durchfuehrungsteile - nomenclature of the lead parts

Pfropfen - plug

Schweissnaht - weld seam

kurze Huelse - short sleeve

Nut mit Quecksilbervorlage - Groove with mercury adapter

innerer Hohlraum - internal cavity

Lotzone - soldering zone

aeusserer Hohlraum - outer cavity

Frequentarohr - Frequenta tube

Ansatz - shoulder

lange Huelse - long sleeve

Schweisskante zum Anschluss an das Vakuumgefaess - welding edge for connection with the vacuum vessel.

Figure 2: Solder test of Silver- Frequenta AS 42 with strong generation of gas (not reproducible)

Figure 3: Solder test of silver and Frequenta AS 42 with gas bubbles and crystallized silver surface (not reproducible)

Figure 4: Soldering test of silver and Frequenta AS 42 C with slight generation of gas (not reproducible).

Figure 5: First attempt at electrolytic soldering (not reproducible)

Figure 6: Auxiliary electrodes for electrolytic soldering

a) external b) internal electrode

Hilfselektrode (Graphit) - auxiliary electrode (graphite)

Silberelektrode - silver electrode

Figure 7: Potential distribution and current characteristics in Frequenta with different arrangements of electrodes

Hilfselektrode (Graphit) - auxiliary electrode (graphite)

halbe Laenge des Frequ.rohres - half length of the Frequenta tube

Die Zahlenangaben ... - the figures are voltage values in per cent of the total voltage

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Figure 8: Example of the effect of an intermediate electrode on equipotential areas

Zwischenelektrode (Graphit) - intermediate electrode (Graphite)

Die Zahlenangaben... - The figures are voltage values in per cent of the total voltage

Figure 9: Specific ~~permeability~~ resistance of Frequenta as function of temperature

Spezifischer Durchgangswiderstand - ~~specific permeability~~ resistance

Temperatur - temperature

Figure 10: Change of resistance of a graphite auxiliary electrode during heating to soldering temperature (measured between the front end areas of a Frequenta tube of 16.5 mm internal diameter and 70 mm length)

Widerstand - resistance

a) graphite paste properly mixed

b) graphite paste containing too much binder

Figure 11: Various graphite plugs (electrical connection of the auxiliary electrode) (Not reproducible).

Figure 12: Test arrangement for measuring HF emission

Zum 400 V Gleichstromgerast - to the 400 v DC set

Beobachtungsfenster - observation window

Isolierte Einfuehrung ... - insulated lead-in of the cooled electrode with water supply and drain

Abschirmbleche - shields

Quarzzylinder - quartz cylinder

gekuehlte Elektrode - cooled electrode

Eisenrohr - iron tube

Untersatz aus Eisen - iron base

Graphit-Gluehkoerper - graphite incandescent body

Vakuumofen (Gefaess) - vacuum furnace (vessel)

Kuehlwasserbassin - cooling water tank.

Figure 13: Measurement of emission on Frequenta AS A2

gekuehlte Elektrode- cooled electrode

Temperaturmesspunkt - temperature measuring point

Graphitanstrich - graphite coating

Ofentisch - furnace plate

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Messanordnung in natuerlicher Groesse - measuring arrangement in natural size

Emissions-Strom - emission current

Kalte Elektrode , negativ - cold electrode, negative

Kalte Elektrode, positiv - cold electrode, positive

Figure 14: Measurement of emission on iron St. 45.29. Measuring arrangement in natural size.

gekuehlte Elektrode - cooled electrode

Tempe-atur-Messpunkt - temperature measuring point

Eisenrohr - iron tube

Ofentisch - furnace base

Emissions-Strom - emission current

Kalte Elektrode,negativ - cold electrode, negative

Kalte Elektrode,positiv - cold electrode, positive

Figure 15: The course and the effect of electrolysis of Frequenta in a vacuum

Anionen - anions

Kationen - cations

dunkelbraune A-Schicht - dark brown anode layer

hellbraune A-Schicht - light brown anode layer

braune K-Schicht - brown cathode layer

schwarze K-Schicht - black cathode layer

Figure 16: Dissociation of Fe_2O_3 in a cation and complex ion

Silberelektrode - silver electrode

Graphit-Hilfselektrode - auxiliary graphite electrode

Figure 17. Conversion of the external Frequenta layer after several hours of annealing in air at 600°C

Figure 18: Line sondes on a parallel bundles of flux lines

Strichsonde- line sonde

Figure 19: Line sondes on vertically scattering bundle of flux lines

Hilfselektrode - auxiliary electrode

Strichsonden - line sondes

Figure 20: 400 V DC set.

1 - Transformer 220 V / 2 x 400 V

2- Transformer 220 V/ 2 x 2 V

3 - Rectifier tube

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4 - Electrolyte condenser

5 - Filter choke

6 - Rotary-coil voltage meter

7 - Rotary-coil ammeter

8 - Shunt for measuring range

9 - Push-button switch for disconnecting shunt

10- 1 amp. fuse

11- 0,9 amp fuse

12- single-pole switch

13- potentiometer

14- single-pole switch, coupled with potentiometer

15 - resistance

16 -resistance

Figure 21: DC set for 400v, 200 ma (not reproducible)

Figure 22: Soldering racks for electrolytic soldering of leads of 16,20, and 42 mm diameter. (Not reproducible)

Figure 23: Soldering holders and rack for electrolytic soldering

Oeffnung fuer pyrometrische Temperaturmessung : opening for pyrometric temperature measurement

Drahtanschluss - wire connection

Kontaktflaeche - contact surface

Kontaktstern - contact star

Loeteinsatz - soldering holder (containing 4 leads of 52 mm diameter)

Keramische Saeule - ceramic column

Quarz-Zylinder - quartz cylinder

Abschirmbleche - shields

Dreiarmiger Fuss - tripod base

Rohrzwischenlage - tubular intermediate layer

Figure 24: Insulated lead-in for the vacuum furnace

Glasscheibe - glass pane

Gummidichtung - rubber packing seal

isolierter Ring - insulated ring

Anschlagring - stop ring

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Kontaktrohr-Fuehrung - contact tube guide

Anschlagstift - stop pin

Ofendeckel - furnace cover

Abschirmbleche - shields

Kontaktstern - contact star

Hilfselektroden-Zufuehrung - auxiliary electrode lead

Keramische Saeule - ceramic column

Figure 25. Diagram of the electrolytic cold ring of a lead of Frequenta AS 42 C, diameter 29 mm, length 70 mm.

Widerstand - resistance

Elektrolytstrom - electrolytic current

Temperatur - temperature

Heizstrom aus - heating current off

Zeit - time

Figure 26: Diagram of the electrolytic soldering of a lead of Frequenta AS 42 C, diameter 52 mm, length 95 mm.

Legend same as above.

Figure 27: Diagram of the electrolytic soldering of a lead of Frequenta AS 42 , oxidized and burned, diameter 60 mm, length 50 mm.

[redacted] Legend same as above.

Figure 28: Resistance of a lead without soldering metal as function of time, temperature and pressure (Frequenta AS 42 C, 29 mm diameter).

Gaseinlass - admission of gas

Other legend same as above.

Figure 29: Diagram of the electrolytic treatment of a lead without soldering metal (Frequenta AS 42 C, 29 mm diameter).

Legend same as above.

Figure 30: Electrolytic solder sample, Silver- Frequenta AS 42 C (not reproducible).

Figure 31: Electrolytic soldering with flaw in the silver (not reproducible).

Figure 32: The surface tension forces during hard soldering.

Eisenflaeche mit Talkum-Anstrich - iron surface coated with talcum

Frequentaflaeche - Frequenta surface

Eisenflaeche blank - iron surface, blank

Normal-Loetung - normal soldering

Elektrolytische Loetung - electrolytic soldering

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