E. V. J. - No. 51 - May 1954 - pp. 75-80

No. 251 - PRODUCTION OF A FLAT OXIDE-COATED CATHODE BY SPRAYING AND MEASUREMENT OF SURFACE ROUGHNESS

Y. NAKAMURA, S. OKADA and Y. KATO
Electrical Communication Laboratory, Tokyo, Japan

1. INTRODUCTION.

In planning the construction of a high-frequency triode for operation at 4,000 mc/s we always encounter the problem of producing a cathode with an extremely flat surface. In such a triode, the grid-cathode spacing is in the order of 10 to 40 microns, and the maximum deviation from flatness, including surface roughness, must be less than 10% of this value.

It is possible to use a metallic cathode such as the L cathode, and we have already succeeded in constructing such a cathode in our laboratory, but the high temperatures required by this cathode make it difficult to build the grid-cathode assembly, and we were led to abandon it for our purposes.

In using an oxide-coated cathod we find that the electrophoresis method gives us a surface with very little roughness, but on the other hand rather wavy, and we have therefore tried to find a method of coating by spraying which produces a cathode surface which is flat within 1 or 2 microns. We also tried, later, to reduce wastage of the carbonate mixture by using electrostatic spraying.

2. PARAMETERS WHICH AFFECT SURFACE QUALITY.

In order to obtain consistent surface quality, the spraying conditions must be held constant. Among the various parameters, we cite the following as the most important:

a) Degree of fineness obtained by ball-mill grinding

b) Composition of the emissive paste.

c) Relative positions of the spray gun and the specimen to be coated.

d) Air pressure at the gun.

2.1 Pulverization by grinding.

It is obvious that the carbonate powder must be as fine as possible. But prolonging the ball-mill grinding

does not produce a proportionate increase in fineness. Harasima (1) has shown that grinding for 40 to 50 hours is sufficient. We have obtained similar results.

For the paste, we use a triple carbonate in order to obtain the best thermionic emission. This carbonate, after the prescription given by Amakasu (2), is drawn from a mixture of three nitrates, composed of: $Ba(NO)_2$ $Sr(NO)_2$ $Ja(NO)_23H_2O$ inthe ratio of 47:43:10

The precipitation is made, in the first phase at 20°J. from a solution having a concentration of 0.25 mole, but later at a temperature of 80°J. from a saturated solution.

The carbonate thus obtained is mixed with amyl acetate, and then sent to the ball-mill for 30 hours, also for several hours before using. Sometimes we also use ultrasonic treatment.

The grains of this carbonate are forked or fan-shaped. The effective diameter is less than 0.1 micron for the smallest grains and around 1 to 2 microns (with an average value of 2 microns) for the ordinary grains. If the suspension is retained for some time it settles out, but the grains are easily broken down to the values given above by grinding for a short time.

In order to obtain a paste of fine particles, we let the solution stand for twenty or thirty minutes, and then use the upper part of the suspension.

2.2 Spray Jet

2.2.1 Jonstruction of the spray gun. In a commercial spray gun the level of the paste is above the nozz le, so that the drop of paste always remains at the nozz le when the trigger is not pressed. The drop evaporates readily, and the residue thus formed blocks the nozzle.

In order to overcome this difficulty, we have constructed another type as shown in Fig. 1. In this type, when the flow of air is stopped, the liquid returns to the tank and thus no residue is produced at the nozzle. The spraying obtained is as good as from the first type.

2.2.2 Observations on the carbonate grains. Small pieces of glass or nickel were placed in the cone of the jet in various positions. These pieces were exposed to the jet for very short times, determined by a falling shield placed in front of the gun.

If the pieces of glass are lightly covered with oil, the falling drops do not spread as much, and after they are dry one can observe the grains which were suspended in each drop. (Fig. 2)

The distribution of the effective diameter of the grains thus observed in the drops is shown in Fig. 2. The majority of the diameters falls below 5 microns. This value agrees reasonably well with that described in section 2.1.

2.3 Air pressure for spraying.

The air pressure has a marked influence on the size of the drops in the jet, as has been described by many authors. Briefly, high pressure gives small diameter drops. We have obtained the same results in our experiments.

Notice, however, that we do not consider the size of the drops in the main stream, but rather the grains of carbonate within the drops. We can evade the much-discussed but unresolved problem of the distribution of the drops in the cone of the jet.

We choose the pressure so as to obtain stable intermittent spraying and sufficiently small drops. Too high a pressure (for example 60 kg/sq.in.) is too hard to form a stable cone. On the other hand, too low a pressure, for example 20 kg/sq.in., gives drops which are too large. We have established a value of around 40 kg/sq.in. as the optimum value.

2.4 Exposure time

By direct observation of the surface under the jet or the surface after the shutter is closed, and by variation of the exposure time, we can see the process of coating and of drying.

The surface of the cathode coating remains wet when the concentration of the paste and the gun-cathode spacing are suitable. If spraying is continued, the coating begins to run, which reduces the chances of obtaining a flat cathode; even when the cathode surface is held horizontal.

On the other hand, if the coating is made in a dry condition, the surface becomes rough. The best condition consists of keeping the surface always wet, but not to the point where it begins to run. In order to acheive this condition it is necessary to alternately expose and dry. The optimum exposure time depends on the concentration of the paste (especially that of the nitrocellulose).

The drying is accelerated by raising the temperature of the atmosphere surrounding the cathode. The optimum condition is when drying is complete in 20 to 30 seconds.

2.5 Nitrocellulose Concentration.

Increasing the nitrocellulose increases the viscosity, which in turn has the following advantages and disadvantages:

Advantages:

1. A flatter surface is obtained.

2. A firmer surface is obtained.

Disadvantages:

1. Cracks appear after exhaustion. The edges of the cracks are higher than the surface irregularities.

2. Large cracks appear and cause detachment of the coating.

We must therefore find a compromise between these opposing solutions.

Several pastes of various concentrations of nitrocellulose (at a degree of nitration of 60 seconds) were prepared. After coating the cathodes of test tubes with these pastes the tubes are sealed off and submitted to the exhaustion process. Following this the tubes are brokento obtain the cathodes in order to examine them. The quantity of nitrocellulose (by weight) is from 0.5 to 3 percent.

The optimum value of nitrocellulose is found to be between 1.5 and 2 percent. The thermionic emission does not show any perceptible change when the nitrocellulose concentration varies between these limits.

To determine the nitrocellulose concentration in the upper part of the suspension (which varies gradually as the suspension is allowed to stand), measurement of viscosity seems to be the best method.

3. CONDITIONS ADOPTED AND RESULTS

The experiments described above enable us to establish the spraying conditions for our purpose as follows:

1. Paste: as described in 2.1; the nitrocellulose concentration is set at 1.7 percent.

2. Gun: as shown in Fig.1.

3. Air pressure 40 kg/sq.in.

4. Gun-cathode spacing: 50 cm.

5. Exposure time: 0.3 to 0.5 sec. each time; interval for drying: 20 to 30 sec.; the number of exposures varies according to the thickness desired (for example 18 to 20 times for a thickness of 20 microns)

The photographs show three examples of surfaces (see figs. 3 through 5) and the last one shows a surface completely flat with an accuracy of 2 microns on a metal support of polished nickel, obtained under the given conditions. Fig. 6 shows a typical section of a cathode assembly. The two blocks next to the cathode represent in section the piece of steatite which supports the grid. The surface of this piece was polished at the same time as the metal cathode support, so that the two pieces have one common flat surface.

The flatness and roughness of the cathode surface examined by silhouette lighting are shown for some specimens in 5.

To obtain a better surface, we have tried a method of mechanical planing, which will be published later. Figs.7a and b show an example of the result of this special construction. The central part shows that which is unuseable. The cross-section is clearly shown in Fig. 7b.

4. ELECTROSTATIC SPRAYING

4.1. Explanation of the method

The method described in 3 gives us good results but it has two disadvantages. On the one hand, a large part of the rather costly carbonate is lost, and on the other hand considerable time is required to acheive spraying of the cathode. In order to overcome these difficulties, we have used a special electrostatic spraying technique invented by M. Sakai (3) of the Tyukyo Denki Company.

So-called electronic spraying, in the painting industry, consists of gun spraying, and directing the drops by means of an electric field so as to attach them to the desired electrode. What we propose, however, is completely different. We do not use any gun, but rather we make use of a corona discharge to produce extremely fine drops from the surface of a liquid. The charged drops are carried by electrostatic force into contact with an electrode, in this case the sample cathode.

In the apparatus shown in Fig. 8, A is the paste receptacle, which has a fine, pointed spout, and G is the agitator. If a voltage of 7 to 12 kV is applied between the pointed spout and the object to be coated, on separating the two electrodes by a distance of

about 10 cm. a cone of extremely fine and almost invisible drops is formed.

The shape of the spray cone varies depending on the physical characteristics of the paste, (See Fig. 9a and b). The tip of the spout must be sufficiently pointed to concentrate the electric field, but not so fine that the precipitate will block the opening.

The paste is stirred constantly by the agitator G, but for the most effective agitation the bottom of the spout must be pretty large. Several attempts have been made to find the most convenient shape for the spout, and we have found that the shape shown in Fig. 10 is the best. The angle B may be zero, but if it has a value of 5 to 10 degrees the point always stays conveniently wet. L is the shutter which determines the exposure time and prevents the deposition of the large grains which are often produced at the start of the spraying.

4.2 Choice of the vehicle. The choice of the vehicle has a rather considerable influence on the surface finish. The results for several vehicles usable in practice are shown in Table 1. At present we are using paste No. 6, which gives good results.

The relationship of spacing to voltage is shown in Fig. 11 taking current as a parameter. The surface condition is also shown in this figure. A current less than 0.15 uA gives a poor yield, but anything over 0.7 uA gives too much wetness, which makes for a poor surface quality.

4.3 Characteristics of the coating and the surface. The relationship between quantity of coating and voltage is shown in Fig. 12 for a constant spacing of 15 cm.

For paste No. 5 (see table below), the surface obtained by wet spraying shows little roughness but more waviness, with a total irregularity of $\leq$ 5 to $\leq$ 7 microns (see Fig. 14). For paste No. 6, if a slowly drying spray is used, the surface shows some roughness but it is flat enough. If a slightly wet spray is used, a surface of the same quality is obtained, with an irregularity of the order of $\leq$ 3 to $\leq$ 4 microns.

We give herewith an example of spraying:

Voltage: 10 to 11 kV — Spacing: 5 cm.

Current: 0.31 to 0.43 uA — Shape of spout; Type HB

Agitation: 120 rpm

Exposures: 1st. to 8th.: 3 to 8 secs.

9th. to 16th.: 11 to 45 secs.

Total: 215 secs.

Thickness of cathode coating: 15.5 microns

Surface irregularity: $\leq$ 3.5 microns

The electrostatic spraying method is very effective in economising on carbonate, but produces a lower quality surface than the spraying described in 3. This forces us to use machining for tubes in which the grid-cathode spacing is in the order of 10 microns. We must add that with the electrostatic method, it is much easier to build an automatic machine.

5. MEASUREMENT OF SURFACE IRREGULARITY

5.1. Choice of equipment. If the surface in question is metallic, measurement to an accuracy of 1 micron is not difficult. On the other hand, for a surface of carbonate or oxide, which is easily crushed, there are some limitations which must be placed on the various known possibilities of measurement;

a) The specimen is easily crushed. The measurement pressure must be as small as possible.

b) The specimen must be free from impurities during the measurement.

c) It is necessary to know not only the mean value but also the maximum value of the irregularity.

d) The measurement must be made quickly in order to avoid the effects of dust and moisture in the atmosphere.

After having examined several methods, such as mechanical, optical and pneumatic, we conclude that the silhouette lighting method (Lichtschnittmethode) after Schmaltz (4) is the most appropriate. Unfortunately this method is not applicable for the measurement of irregularities in the order of 10 microns.

5.3. Description of the apparatus. We have tried to build apparatus with an accuracy of better than 1 micron. The design of the optical system is the subject of another disclosure (5), here we shall give only the results of the calculations.

The objective has an aperture number of 0.25 and a magnification of 10x. The eyepiece is of the micrometer type with a magnification of 10x. The smallest scale division of 1 mm in the eyepiece corresponds to a length of 1 micron on the image.

For one edge of the slit F, we use a rectilinear plate (see Fig. 13) with an accuracy of 1.5 micron in a length of 75 mm. The other edge is simply a cylinder of blackened brass. If we apply to the slit F a parallel beam of monochromatic light produced by the source L and the two lenses O_3 and O_2 the slit becomes an extremely sharp, rectilinear light source of which a reduced image is projected by the lens O_1 on to the surface of the specimen T. This image is observed by means of the microscope M. The specimen is movable in two perpendicular directions in a horizontal plane. The angle of incidence α and the angle of emission β are chosen as 45° each in Fig. 13 but these angles may be varied, and sometimes the combination $\alpha = 60^\circ$ and $\beta = 30^\circ$ is used.

To calibrate the equipment, a piece of polished metal, of which the surface is extremely flat, and of which the roughness and flatness have already been measured, is placed on the specimen support. The image was rectilinear within $\pm$ 0.25 micron, which is considered to be the inherent error of the equipment. We can thus measure by means of this equipment all the irregularities of a flat surface with a maximum error of 0.5 micron. There is some increase in the error for a rough surface because of diffusion of the light, but in no case does this exceed 1 micron.

5.2. Examples of the results of measurements. Figs. 14 to 16 show surfaces of various roughnesses: the sample in Fig. 14 has a roughness of 22 microns and that of Fig. 15, 11 microns. Fig. 16 shows the best surface, it having a roughness of 2 microns. In Fig. 7 can be seen pictures of the section and a photomicrograph side by side.

6. CONCLUSION

This research was done with a view to constructing high-frequency triodes, in the Electronic Section, Electrical Communication Laboratories, and the satisfactory results are due to the collaboration of many of the Laboratory personnel.

The authors wish to express their thanks herewith to the personnel of the high frequency triode group, especially to M. T. Miwa, for their co-operation. They sincerely thank M. T. Seki for his constant encouragement during the course of their researches.

TABLE 1.

No.of Paste	Vehicle	Pulver-ization *	Stabil. of Spray	Opt.Curr. uA	Condit. Dry/Wet	Surf. Qual. **
5	Amyl acetate (iso)	Y-Z	Good	0.04-0.07	Dry	C
6	Ethyl Alcohol + Amyl ac. (iso)	Ionical X	Good	0.15-0.3 0.3-0.4 0.4-0.7	Dry Medium Wet	A-B
7	Butyl Alcohol	Y-Z	Good	0.10-0.15	Wet	B-C
8	Acetone + Amyl ac.	Z	Poor	0.01-0.20	Wet	C
9	Acetone + But.Alc.	Y	Poor	0.13-0.23 0.23-0.40	Dry Wet	B

*The degree of pulverization is given by the letters X, Y, and Z, which designate very good, good, and fairly good respectively.

**The quality of the surface is given by the letters A, B, C and D which designate very good, good, fairly good and somewhat poor.

BIBLIOGRAPHY

(1) Harasima, Minobe and Nagao, Nichiden Kido 1, 100, Sept.1951

(2) Amakasu et al., see paper No. 211 of the Congress.

(3) Sakai, Japanese patent.

(4) For a detailed description of this method, see Perthen, "Prufen und Messen der Oberflachengestalt", Munchen, 1949.

(5) Nakamura and Kato, Internal Report, Seika Hokoku, No. 482, of the Electrical Communication Laboratory Tokyo, Japan, Feb. 1954, andin the Journ. Appl. Phys. Japan (now being printed).

Translated from the original French by Peter G. Smee, August, 1957.