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Kinetics of the Deposition of Nickel Onto Powder Surfaces from Solutions of Dicyclopentadienylnickel

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Metal coating of submicron particles is normally carried out in the liquid phase in order to bypass the problems of agglomeration and nonuniform coating. In particular, nickel coating from solutions of dicyclopentadienylnickel has found use in the preparation of nickel coated carbonate crystallites. The objective of this work was to define the effect of suspended powder surface area and surface chemistry on the mechanism and kinetics of nickel deposition, and the texture of the resulting deposits. The system amylacetate/dicyclopentadienylnickel/hydrogen/*S* is characterized, where *S* represents the powder on which the metal deposit is generated. As a simplification, the powder may be regarded as a catalyst in the heterogeneous reaction

$$(C_5H_5)_2\,Ni + H_2 \xrightarrow{S} Ni + 2C_5H_6\uparrow.$$

Kinetic data obtained by sequential sampling of solutions during reaction illustrate the various phases of reaction. A pronounced induction period is observed, and associated with the presence of moisture, the available solid surface area, and the nature of the solid surface. This is followed by a reaction whose rate is controlled by the partial pressure of hydrogen. These observations are related to a proposed reaction mechanism. Scanning electron microscope photographs are included to illustrate the pronounced changes in condition of the nickel deposit which parallel the changes in reaction mechanism.

This work provides guidelines for the preparation of metal coatings by decomposition of solutions of organometallic compounds.

INTRODUCTION

This paper describes a study of the variables which affect the rate and quality of nickel deposits from solutions of dicyclopentadienylnickel (DCPDN). The study extends the preliminary observations (*1*) describing the use of DCPDN for preparing nickel coated (BaSr)CO_3 crystallites for use as cathode coating. It defines the effect of variation in suspended powder surface area, the chemistry of the powder surface, and the effect of moisture on the relative rate of the nickel deposition reaction and the texture of the resulting deposits.

In the normal course of nickel coating a submicron powder, a given quantity of DCPDN is added to a suspension of the powder in isoamylacetate at room temperature. A hydrogen ambient is established, and the mixture heated to 120–125°C in the apparatus illustrated in Fig. 1. The simplest written expression of the decomposition reaction is

$$(C_5H_5)_2\,Ni + H_2 \rightarrow Ni + 2C_5H_6\uparrow,$$

though other organic products are formed, and heterogeneous catalysis by the surface of the suspended powder determines the rate.

Early in the course of the reaction, the clear hydrogen burn-off flame becomes slightly luminous from volatile organic de-

$$(C_5H_5)_2Ni + H_2 \rightarrow Ni + 2C_5H_6\uparrow$$

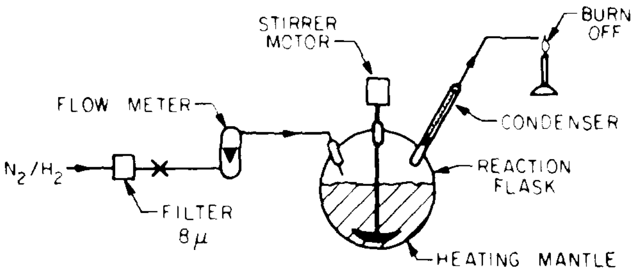

FIG. 1. Coating apparatus.

composition products. Before the organic decomposition product is detected in appreciable quantity at the burn-off, its concentration must exceed its solubility in the isoamylacetate at the reaction temperature. If the reaction temperature, DCPDN concentration, and volume of isomylacetate are constant, the presence of a detectable luminosity in the burn-off flame is reproducible and represents a definite point in the progress of the decomposition reaction. Prior to this study, the elapsed time to this point had been observed to vary widely with concentration of suspended solid and the chemical nature of the powder surface, the limiting case being that of a solution of DCPDN in amylacetate, which appeared stable over long periods in the absence of particulate matter.

Regardless of the time until initiation of reaction the subsequent time to completion appears independent of the nature of the powder surface. The kinetics are readily monitored since DCPDN imparts a brilliant green color to amylacetate solutions, whose disappearance can readily be followed.

EXPERIMENTAL METHODS

The experimental work was divided into three phases.

(1) A semiquantitative study of Ni deposition on a number of different powdered materials, with all other variables such as the concentrations of DCPDN and hydrogen held constant;

(2) An examination of the effect of water content;

(3) A quantitative study of the kinetics of the nickel onto nickel system.

Semiquantitative Studies of Various Powders

The first experiments involved the deposition of nickel onto equivalent surface areas of a number of powders with distinctive surface chemistry. The quantity of each powder used was such as to give a BET surface area of $1.2 m^2/325 cm^3$ of solution. The error inherent in BET measurement varies with the material and the amount of surface involved. This limited this part of the study to a semiquantitative evaluation. 90°C was chosen as the reaction temperature to ensure reaction rates slow enough to measure without sophisticated analytical equipment. Detection of organic decomposition products in the burn-off flame was used to monitor the initiation of reaction. The purification of starting materials is described in Appendix A.

The data from runs with Ni, Al_2O_3, $(BaSr)CO_3$, NiO, and Teflon are illustrated in Fig. 2 and compared to the characteristics of a solution of DCPDN that contained no deliberately added particulate matter. Note that in every case an induction period of variable length preceded a reaction period that was almost constant and that nickel itself, and solution free of particulate matter, appear to represent the limiting cases. The surface area per gram of the available Teflon powder was so low

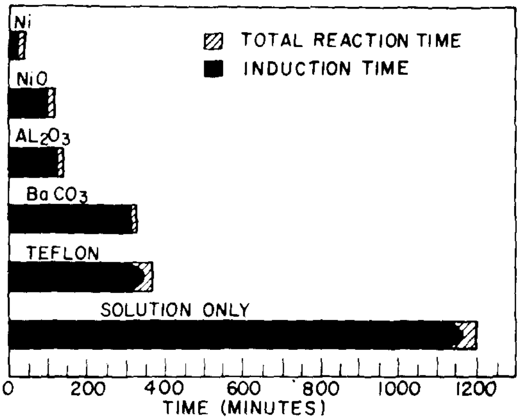

FIG. 2. Effect of surface.

that it proved impractical to get good BET data or add sufficient Teflon to match the surface area of the other powders. Teflon must, therefore, be regarded as quite active.

After this first examination of potentially interesting systems, a study of nickel powder at various concentrations was carried out. The data are presented in Fig. 3 which again gives time until detection of luminance in the burn-off. In this case it is particularly interesting to note a well-defined knee at aproximately 0.1 $m^2/325$ cm^3 of solution.* This separates a high concentration region where total reaction time is essentially constant, from a low concentration region where induction time increases rapidly with decreasing nickel surface area. Time from induction to completion of the reaction remains essentially constant at 15 ± 3 min, as in the case of varied powders.

Effect of Water on the Coating of (BaSr)CO_3 Crystallites

The preparation of both the wet and dry isoamylacetate used is detailed in Appendix A. Analysis showed the water content to be 0.75% for the wet isoamylacetate and 0.085% for the dried isoamylacetate. Each coating run was made with the same quantity of powder having a BET surface area of 120 $m^2/325$ cm^3 of solution.

TABLE 1
EFFECT OF WATER ON NICKEL COATING OF CARBONATE CRYSTALLITES

Isoamylacetate	Detection Time	Reaction Temp (max.)
Dry	42 min.	130°C
Wet	120 min.	130°C
Dry	165 min.	90°C
Wet	>600 min.	90°C

Table 1 illustrates the effect of water on the nickel coating of the (BaSr)CO_3 crystallites. Initiation of reaction was again determined by the onset of luminescence in the burn-off flame.

No attempt was made to maintain the water content during the course of these wet runs other than the refluxing which normally occurs during the coating operation. This was done to simulate the normal or practical conditions used in cathode coating preparation.

From the data, it is evident that the presence of water results in a prolonged induction period. For all practical purposes, the 90°C decomposition reaction was extinguished. However, scanning electron photomicrographs taken of the carbonate crystallites nickel coated from both wet and dried isoamylacetate at 130°C revealed no detectable difference between them. There is also no evidence of any appreciable colloidal nickel formation in these coating runs.

Quantitative Studies

The system nickel onto nickel powder was chosen for kinetic studies, since it was already evident that there were interesting variations with initial concentration. Two points were selected from Fig. 3, 1.5 $m^2/325$ cm^3 solution and 0.005 $m^2/325$ cm^3 solution, above and below the knee. A Beckmann DK-2 spectrophotometer was used to follow the decrease in the 6900 Å absorption peak characteristic of DCPDN. Samples were extracted from a modified reaction flask which allowed insertion of a long hypodermic needle without significant contamination with oxygen, or danger of

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* In this case, the precision of the BET determination was estimated to be 0.10 ± 0.05 m^2/gm. All subsequent kinetic measurements are relative, based on weight of powder added.

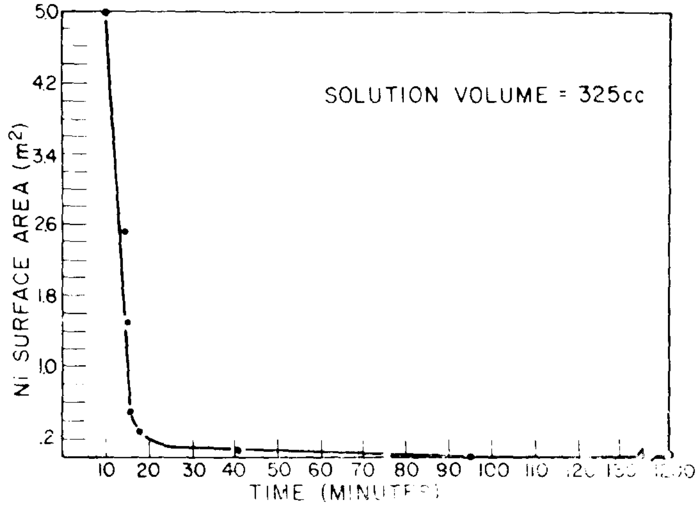

Fig. 3. Reaction time vs nickel surface area.

explosion consequent on suck-back of the flame at the burn-off. Prior to sampling, the hypodermic was cleaned, dried, and flushed twice with nitrogen. After withdrawal, the sample was injected into a sample bottle previously flushed with nitrogen, and quenched by immersing the sample bottle in ice water. Samples were then maintained by storing above liquid nitrogen in a dewar until the run was completed, and time was available for spectroscopy. With samples taken early in the run, there was very little interference due to light scattering by colloidal particles, but in the 0.005 m^2 run, it was necessary to centrifuge the samples prior to the check for residual DCPDN due to finely divided nickel formed during the reaction. Data from the two runs are shown together in Fig. 4. It is intriguing to note that the induction period appears to be a period of complete inactivity, while the reaction rates are identical. The data have been assembled to create one composite of the form indicated so that the identity of the slope to the pseudo zero-order reaction region is highlighted.

One other run was carried out at 1.5 m^2 nickel surface/325 cm^3 solution with the concentration of hydrogen reduced by substituting 10% forming gas for the undiluted hydrogen of the previous runs. Figure 5 shows that once again the reaction was pseudo zero order. While the induction period remained very short, the reaction proceeded more slowly, with a rate that

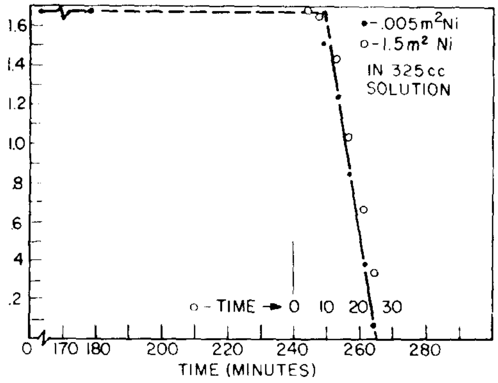

Fig. 4. Reaction rate vs surface area.

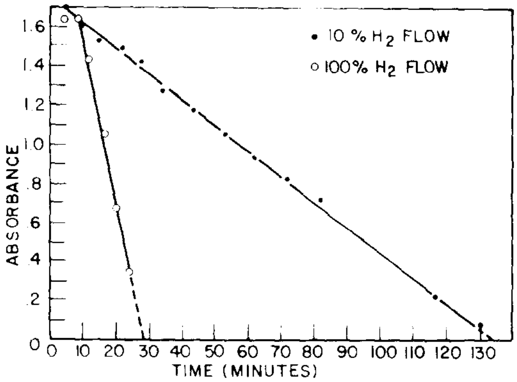

Fig. 5. Reaction rate vs hydrogen concentration.

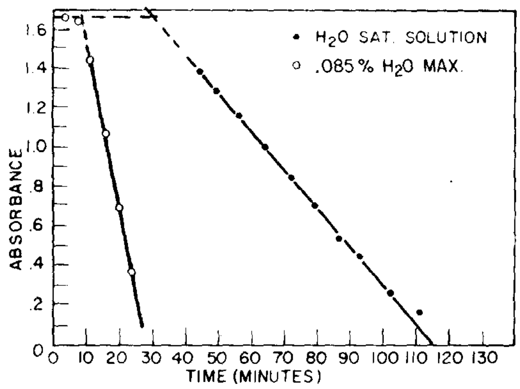

FIG. 6. Reaction rate vs water content.

clearly reflects the change in partial pressure of hydrogen above the solution.

The kinetics in water-saturated isoamylacetate are represented by Fig. 6. Water saturation was maintained during this reaction by passing the hydrogen through a water bubbler prior to entry into the reaction flask. A 1.5 $m^2/325$ cm^3 solution of nickel powder surface was used, which is a surface concentration well above the knee of Fig. 3. There is an induction period of about 30 min before the reaction proceeds which is undoubtedly caused by the presence of water. The reaction also proceeds more slowly than the corresponding "dry" reaction.

Scanning Electron Photomicrographs

In order to evaluate the effects of various aforementioned parameters on the quality or texture of the nickel deposit, scanning electron photomicrographs were taken of the powders. The first S.E.M. photograph in Fig. 7 illustrates the detail of the nickel powder surface used in the subsequent experimental runs. The magnification is 10K. Note that the surface is only gently undulating in appearance with no sharp edges or protrusions, and there is no evidence of crystallinity (see Appendix A). The next photomicrograph, Fig. 8, is also at 10K magnification. This is nickel powder, nickel coated during a "dry" run with an initial nickel powder surface area of 5 $m^2/325$ cm^3 solution. There is virtually no distinction in surface texture from the original powder surface. It is important to note that there are a very few 1000–2000 Å diameter particles present on the powder surface which represent a small quantity of colloidal nickel formed during the reaction.

The nickel coated surface from the experimental run using 0.25 m^2 in 325 cm^3 solution, Fig. 9, is dramatically different from the surfaces seen in Figs. 7 and 8. In addition to what appears to be a somewhat rough nickel coating, there are a great quantity of adherent nickel particles in the 500–10,000 Å size range. Their spherical shape strongly suggests that they grew in solution and adhered to the larger particles during the later stages of the reaction. Figure 10 helps to clinch this: it shows the colloidal nickel formed in the decomposition of DCPDN solutions containing no deliberately added particles. Note the similarity in shape, and slightly greater average size when compared to the overgrowth of Fig. 9.

Figure 11 shows a nickel surface coating which seems to be porous and granular. This deposit was the result of reaction in 10% forming gas. Figure 12 shows that one may obtain the same effect by working with surface concentrations in between these represented by Figs. 8 and 9. In both cases the porosity of the deposit is set by the relative probability of forming metal clusters in solution, and occluding these clusters in the growing coating on the original particles.

DISCUSSION

A restatement of the observations made during the experimental work is helpful in providing the basis for a plausible reaction mechanism:

(1) The reaction is heterogeneous.

(2) With high concentrations of active surface (>0.1 $m^2Ni/325$ cm^3 solution), there is no observable induction period.

(3) With low concentrations of active surface (<0.1 $m^2Ni/325$ cm^3 solution), there is an induction period whose duration is inversely proportional to the amount of active surface.

FIG. 7. Scanning electron microscope (S.E.M.) photograph of nickel powder as received.

FIG. 8. The S.E.M. photograph of nickel coated powder. Initial surface area, 5 m^2.

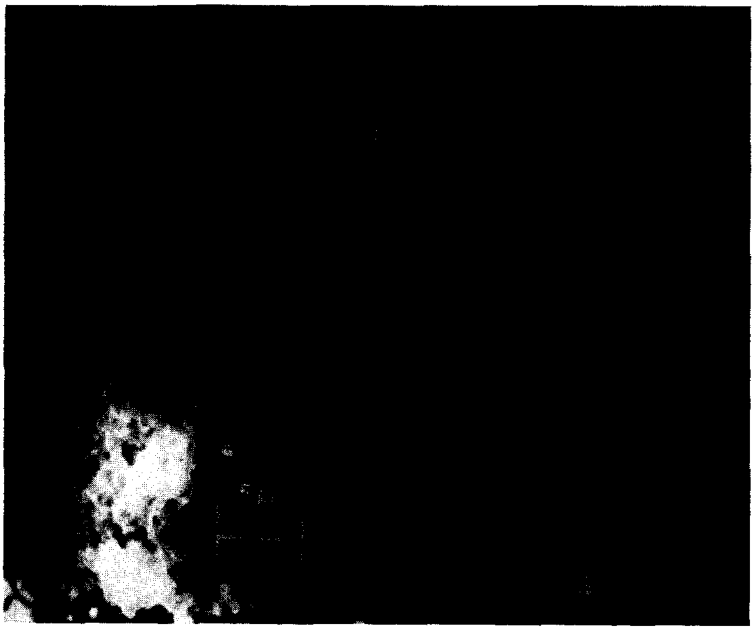

FIG. 9. The S.E.M. photograph of nickel coated powder. Initial surface area, 0.25 m^2.
FIG. 10. The S.E.M. photograph of colloidal nickel from DCPDN decomposition.

(4) The rate of reaction is limited by the partial pressure of hydrogen.

(5) The rate of reaction is unaffected by the length of the induction period.

(6) The induction period appears unaffected by the concentration of hydrogen.

(7) S.E.M. photomicrographs show that visible colloid forms in inverse proportion to the available surface area. The colloid particles eventually adhere to the

FIG. 11. The S.E.M. photograph of nickel coated powder. Initial surface area 1.5 m^2—10% forming gas ambient.

FIG. 12. The S.E.M. photograph of nickel coated powder. Initial surface area, 1.5 m^2—100% hydrogen ambient.

surface of a larger particle, and may then be bound into a coarse, granular coating by further nickel deposition.

We believe that there are not too many mechanisms consistent with these facts, and propose the following argument, which may be used to correlate all the facts observed so far. The induction period is completely quiescent. Within experimental error on the spectrometer the DCPDN concentration remains constant, and changing the partial pressure of H_2 by an order of magnitude has no effect. This is an indication that the "happening" which is making way for reaction does not involve these reactants in the rate limiting step.

In the low solid surface area region, the duration of the induction period is inversely proportional to the concentration of active surface, while above a nickel powder surface area of $\sim 0.1\ \mathrm{m^2/325\ cm^3}$ solution, the induction period becomes vanishingly small. This suggests that the amylacetate solution of DCPDN contained a limited quantity of a specie which absorbed on catalytically active sites. It would have to be present in sufficient quantity to blanket all the active sites in the low surface area experiments. This thesis suggests that the hypothetical absorbent must be reduced in surface concentration to the point where active sites are exposed, before the nickel deposition reaction will begin. It is, therefore, unreasonable to suppose that the absorbent is either DCPDN, amylacetate, or one of the products of their solution equilibria. If it were not for the data illustrated in Fig. 6, it would be reasonable to consider water as the most qualified absorbent. This figure shows that water does have a marked effect, slowing the rate of the reaction, and giving rise to an induction period at a substrate surface area where one would not normally be expected. However, the reaction does proceed in the usual format in the presence of excess water, and we cannot presume water *per se* has been reduced in concentration at the surfaces involved.

If we suppose the involvement of water is in the role of a suppressant, rather than a primary reactant, we find that clean-up of surface oxide becomes a possible induction mechanism:

$$\mathrm{NiO/O} + \mathrm{H_2} \rightleftarrows \mathrm{NiO} + \mathrm{H_2O},$$
$$\mathrm{NiO} + \mathrm{H_2} \rightleftarrows \mathrm{Ni} + \mathrm{H_2O}.$$

This is obviously a great oversimplification, but it would explain our observations. The rate of reduction of surface oxide films by hydrogen would be reduced by the presence of water, and proportional to

$$[\mathrm{NiO}_n][\mathrm{H_2}]^n/[\mathrm{Ni}][\mathrm{H_2O}]^n$$

This implies a strong dependence of rate, and hence duration of the induction period, on the solution concentration of hydrogen and water. In practice, no change in the induction period was noted upon substituting 10% forming gas for 100% hydrogen (Fig. 5). However, these runs were carried out "dry", and the induction period was so short that changes would not have been obvious. The effect of trace water on the induction period may be accentuated by absorption on the solid surfaces prior to the first exposure to hydrogen (Fig. 6).

The region above the knee of Fig. 3 which does not exhibit an induction period is, therefore, explained as the region in which the effective surface concentration of water becomes insignificant compared to the concentration of surface oxide. The implication is that reducing the concentration of water will move the knee toward progressively lower concentrations of nickel surface. We have considered experiments which might "prove" this thesis. Runs with perfectly dry solutions of oxide-free nickel would in theory do so, but in practice, such experiments are extremely difficult to carry out unambiguously. We have not attempted them since our primary purpose was the correlation of reaction conditions and the properties of the product in a practical environment.

CONCLUSION

It can be concluded from this study that the decomposition of dicyclopentadienylnickel is heterogeneously catalyzed by added powder surface. All nickel coating runs were characterized by a quiescent induction period which varied in duration in the order Ni < NiO < Al_2O_3 < $(BaSr)CO_3$ $\ll$ reaction vessel only. This induction period was followed by a relatively short reaction period which was independent of the substrate composition.

More detailed examination of the reaction occurring in the presence of nickel powder has shown that at nickel surface areas below 0.3 m^2/liter, the duration of the induction period is inversely proportional to the nickel powder surface area. The demarkation between the induction period and the reaction is shown to be extremely sharp. The reaction is found to be pseudo zero order, rate limited by the supply of hydrogen. Increasing moisture content is found to extend the duration of the induction period and decrease the rate of reaction. A reaction mechanism is proposed which is consistent with the observations.

The S.E.M. photographs illustrate a pronounced variation of the texture of the deposited nickel with the reaction conditions. This is explained as a consequence of variation in the amount of colloidal nickel incorporated into the deposit. In particular, it is clear that autocatalytic reactions such as the hydrogen reduction of DCPDN solutions will only give smooth coherent coatings when the ratio of substrate surface to solution is high.

ACKNOWLEDGMENTS

The authors wish to express their appreciation of the excellent S.E.M. photographs provided by Mrs. M. A. Giles.

APPENDIX A

The DCPDN was purified prior to use by vacuum sublimation as described in a previous publication (*1*). This purification procedure minimizes the inclusion of the oxidation product of DCPDN which is insoluble in isoamylacetate, and a potential source of catalytic surface. It is normally formed during prolonged storage.

The as received isoamylacetate was purified by fractional distillation. The fraction retained for use had a boiling range of 139–140°C. This boiling fraction was collected in a flask containing BaO pellets to ensure minimum water content in the isoamylacetate. Just prior to use, the isoamylacetate was centrifuged to remove any BaO or $Ba(OH)_2$ particles which may have formed. This procedure was established, because even certified isoamylacetate as received varied from lot to lot in water content. While this "drying" operation did not yield absolutely dry isoamylacetate, it did ensure material which was consistent in water content for the "dry" experimental runs. Karl Fischer analysis showed the water content to be 0.085% by weight.

In addition, prior to the "dry" runs, all powders were heated in the reaction flask to 110°C overnight with a dry (—65°C max dew point; <5.5 ppm H_2O) nitrogen purge to remove absorbed water.

For experimental runs requiring water saturation, isoamylacetate as prepared above was shaken with an equal volume of deionized water and allowed to stand overnight. The isoamylacetate was then decanted prior to use. Analysis showed the water content to be 0.75%.

The reaction vessel and stirrer, after acid cleaning, were thoroughly rinsed with filtered deionized water, filtered acetone, and blown dry using filtered dry air to minimize introduction of foreign particulate matter into the experimental runs which might be a potential source of catalytic surfaces.

Sherritt Gordon nickel powder was used in these experimental runs. It was prepared by aqueous precipitation which implies that the material is amorphous rather than crystalline.

REFERENCE

1. PLEASS, C. M., AND SCHIMMEL, D. G., "A Simple Non-Toxic Route to Coated Powder Cathodes," IEEE Conf. Record of 1968 Conference on Tube Techniques.