

is equivalent to 4-100-400 atomic layers upon the geometrical surface. Minute amounts of metal appear largely to saturate the active surfaces from which electrons are emitted. These may be the surfaces either of nickel or oxide particles. Further addition of active metal contributes little to thermionic activity, but provides a reservoir of active material.

Previous analyses of free alkaline earth metal in vacuum tubes are reported by Berdennikowa,<sup>12</sup> Clausing<sup>4</sup> (p. 348), and Fritz.<sup>13</sup> The water vapor method of Berdennikowa does not discriminate between active metal in the filament and elsewhere in the tube. The same criticism seems to apply to Clausing. Barium nitride formation and microanalysis, as employed by Fritz, appear selective but less sensitive. His results are equivalent to 5-15 micrograms of barium per tube.

The greater amounts found in our experiments we believe to indicate an increased retention, which may be adsorption upon or alloying with the finely divided nickel, and which may also be a factor in a very long useful life obtained with this type of coating. The contrary opinion, that barium is dissolved in barium oxide, has some support from the work of Schriel,<sup>14</sup> who reports a slight solubility, though no evidence for solution under vacuum conditions. From the overall composition, as shown in Table V, we con-

(12) T. P. Berdennikowa, *Phys. Z. Sowjet.*, **2**, 77 (1932).

(13) H. Fritz, *Mikrochemie*, **17**, 191 (1935).

(14) M. Schriel, *Z. anorg. Chem.*, **231**, 313 (1937).

clude that the active metal is somehow dissolved, a conclusion further substantiated by the long time, upward of two hours, necessary to leach out the active metal in the carbon dioxide treatments.

TABLE V

Coating composition (referred to outside surface of coating)

SrO = 984  $\mu$  g./sq. cm.

BaO = 923  $\mu$  g./sq. cm.

Ni = 71.5  $\mu$  g./sq. cm.

Active metal = 0.6 - 65  $\mu$  g./sq. cm. as Ba

### Summary

Using a filament coated with a colloidal mixture of barium oxide, strontium oxide, finely divided nickel, and free alkaline earth metal, we have investigated the quantitative relation between thermionic emission and the content of active metal. A high level of activity was found from 15  $\mu$  g./sq. cm. to 60  $\mu$  g./sq. cm. of equivalent Ba, with a slight apparent maximum at 30  $\mu$  g./sq. cm. where the thermionic current at 1050°K. is 600 m. a./sq. cm. The electron work function is 1.37 v.

The radiant emissive power at 0.66  $\mu$  is approximately 64%, independent of the content of active metal.

The free alkaline earth metal was determined by oxidation with carbon dioxide and analysis of the gaseous reaction products,

NEW YORK, N. Y.

RECEIVED AUGUST 29, 1938

[CONTRIBUTION FROM THE ANALYTICAL LABORATORIES OF FORDHAM UNIVERSITY]

## A Modified Method for the Preparation of Monochloropentamminocobaltic Chloride (Purpureocobaltic Chloride)

BY WALTER A. HYNES, LEO K. YANOWSKI AND MORRIS SHILLER

Monochloropentamminocobaltic chloride, or purpureocobaltic chloride,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , is one of the earliest and best-known of the cobaltamines. During the course of work on the application of such complexes to the microscopic detection of anions,<sup>1</sup> it became necessary to prepare relatively large amounts of this substance in a pure state.

Purpureocobaltic chloride has been prepared and its constitution studied by numerous investigators<sup>2</sup> since its initial synthesis in 1851. These

(1) W. Hynes and L. Yanowski, *Mikrochemie*, **23**, 1, 143 (1937).

(2) "Gmelins Handbuch der anorganischen Chemie," 8 Aufl., 58B, Berlin, 1930, pp. 151-159.

workers used air or pure oxygen as chief oxidants and cobaltous carbonate as the usual source of cobalt.

The chief objections to the older method of preparation are the length of time required for the preparation of the substance, the low yield of pure substance obtained and the impurity of the final product. The low yield and relative impurity of the final product obtained by the usual method are due to the presence of hexamines and other cobaltamines, only removable by repeated recrystallizations or by precipitation from cold

aqueous solutions by acid, followed by separate washings with alcohol and ether.<sup>3</sup>

To obtain approximately 10 g. of pure purple chloride by the older method required an average of about forty hours due to time required for aeration, evaporations and extractions, whereas by our method we can obtain an average of 35 g. of pure salt in not more than five hours.

### Experimental

Forty grams of coarsely ground crystalline cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , is added to a mixture of 50 ml. of water, 100 ml. of concentrated (28%) ammonium hydroxide and 100 g. of solid ammonium chloride in a flat porcelain dish. Twenty-five ml. of 30% hydrogen peroxide is added to this mixture with continuous stirring. The dish is then heated on the steam-bath for one hour. The paste obtained at this point is treated with 500 ml. of 3 *N* hydrochloric acid and heated, with continuous stirring, over the free flame to not more than 60°. The mass is filtered and washed with approximately 150 ml. of 2 *N* hydrochloric acid. The residue is suspended in 1500 ml. of 1.2 *N* ammonium hydroxide and heated to not more than 60° with continuous stirring, when all the purple chloride will be dissolved. This liquid is filtered immediately, the filtrate transferred to a 3000-ml. beaker, placed on the water-bath, and 1500 ml. of concentrated hydrochloric acid added in three 500-ml. portions at fifteen-minute intervals, stirring during each addition, and the heating continued for thirty minutes after the last addition, a total time of one hour. The liquid is filtered while still warm and the residue first washed thoroughly with 2 *N* hydrochloric acid, then with 95% alcohol until there are no further traces of hydrochloric acid in the washings and finally with four to five 25-ml. portions of ether. The residue is then dried for one hour in an oven previously raised to 60°. The yield at this point averages 34 g., equivalent to 85% of the theoretical value. The salt requires no further purification for use as a microscopic reagent or in the preparation of other compounds.

The material was analyzed for nitrogen by both micro Dumas and macro Kjeldahl, for cobalt by semi-micro determination as sulfate, and for total chlorine by the micro

(3) F. Garrick, *Nature*, **136**, 1027 (1935); *Z. anorg. Chem.*, **224**, 27 (1935).

Pregl method,<sup>4</sup> and the following values were obtained.

	Nitrogen		Cobalt	Chlorine
	Dumas	Kjeldahl		
Calculated		27.96	23.53	42.47
Found	27.99	27.91	23.62	42.56
	28.04	27.89	23.62	42.59

Although several investigators have employed hydrogen peroxide as an oxidant in preparing cobaltic compounds,<sup>5</sup> none has specified that this substance may be used as the oxidant in preparing the purple chloride.

A single 1500-ml. volume of 1.2 *N* ammonium hydroxide, about one-half that used in the ordinary method, was employed as solvent to avoid numerous extractions. Heating in ammoniacal solution at 60° hastens conversion of the purple to the aquo salt, this temperature being quite safe, as shown by Lamb and Marden.<sup>6</sup> The converse transformation to the purple is well known, but it was deemed advisable to add the acid slowly with stirring to prevent any possible occlusion of roseo chloride by the purple salt.

We have noticed that the thoroughly dried purple chloride is non-hygroscopic, while a sample which had not been oven-dried tended to gain weight on exposure to air.

Acknowledgment is made to the Works Progress Administration for the City of New York for assistance rendered under Project No. 465-97-3-120.

### Summary

1. Purplecobaltic chloride has been prepared from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  using hydrogen peroxide as oxidant in the presence of ammonium chloride.

2. The product is obtained in much better yield and in a much shorter time than is required by the ordinary method.

NEW YORK, N. Y.

RECEIVED MARCH 8, 1938

(4) We are indebted to Mr. J. Alicino for the micro Dumas and Pregl values.

(5) A. Carnot, *Bull. soc. chim.*, [4] **21**, 212 (1917); R. Durrant, *J. Chem. Soc.*, **87**, 1781 (1905); C. Duval, *Compt. rend.*, **191**, 615 (1930); G. Morgan and J. Smith, *J. Chem. Soc.*, **121**, 1956 (1922).

(6) A. Lamb and J. Marden, *THIS JOURNAL*, **33**, 1873 (1911).