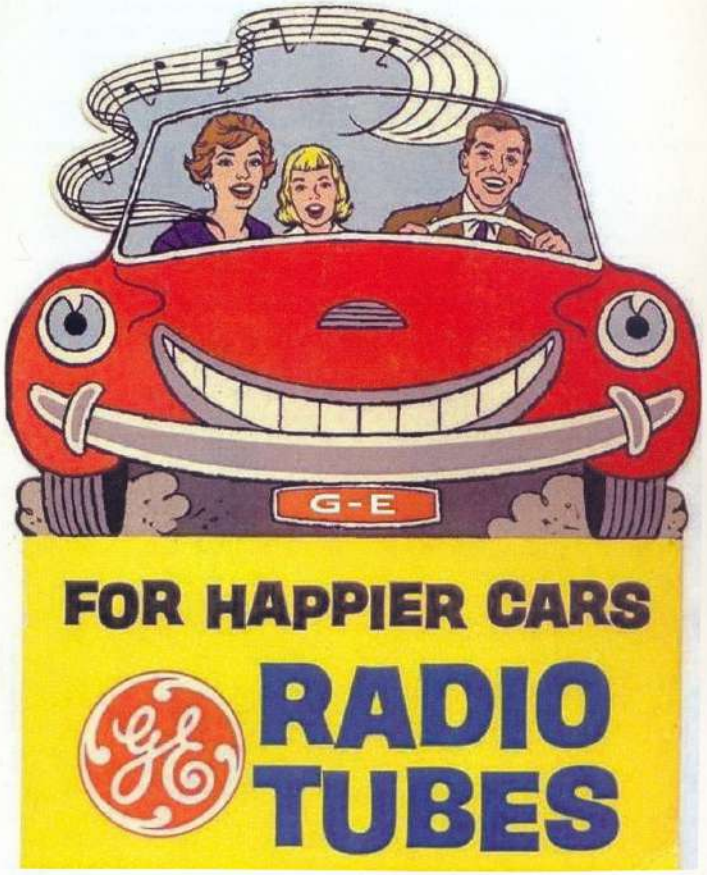
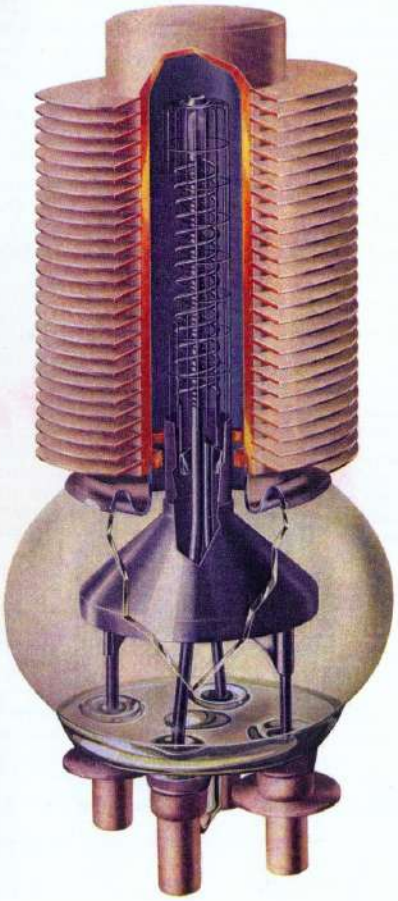


TUBE COLLECTOR

TUBE COLLECTORS ASSOCIATION

"HISTORY • PRESERVATION • APPLICATION"

Vol. 14 No. 6 December, 2012



TUBE COLLECTOR

TUBE COLLECTORS ASSOCIATION, INC.

PO Box 636, Ashland, OR 97520, USA

The Tube Collectors Association is a nonprofit, noncommercial group of individuals active in the history, preservation, and use of electron-tube technology. *Tube Collector*, its bulletin, appears six times per year.

To join TCA: annual dues is $20.00 (in North America; $25.00 elsewhere. Payment by PayPal is welcomed, to *tca@jkasystems.com*. If using a check or MO, please make it payable to "Tube Collectors Association" and mail to the address above. The membership year runs January-through-December. Those joining after February receive the year's back issues of TCA publications. Multi-year membership is invited, at: in North America, $37 for two years or $54 for three; elsewhere, $49 for two years or $73 for three.

Articles on tube topics are welcomed. Editorial correspondence should go to the editor at *tubelore@jeffnet.org* or **102 McDonough Rd., Gold Hill, OR 97525**.

Renewals. inquiries, changes of address, and other membership business should go to Bob Deuel at *k2glo@jkasystems.com* or **PO Box 636, Ashland, OR 97520**. Please use these addresses for inquiries or correspondence rather than the "*tca*" email address above.

FRONT COVER: The Philips TBL6-4000 air-cooled triode for industrial RF heaters, rated for continuous dissipation of 1.3 kW. Its "EIA" identity is 7753, as registered by Amperex in 1960.
From J. Haantjes and H. Carter, Classification of Electron Tubes, 2nd ed. (New York, Macmillan, 1962), courtesy Bro. Patrick Dowd

REAR COVER: A General Electric dealer placard. Original copy is about 8-½ x 11" size.
Deuel Collection

MICROPHONICS FROM THE EDITOR

DEPARTMENT OF CORRECTIONS

In the last issue, we somehow reported that Norm Wilson has been re-elected as TCA vice president. Well, not so: the electee was John Walker, well known tube collector. Our apologies to both parties. Meanwhile, Norm continues to serve artfully as TCA Webmaster.

2013 CHARLOTTE MEET SCHEDULED

The CC-AWA Charlotte event for 2013 is scheduled for Thursday through Saturday, March 21-23. Some details are available at publication time at www.antiqueradiocharlotte@homestead.com. This is a well reputed, well recognizeed meet of long standing. 2013 should be another good year. The special theme will be "Homebrew and Kit Radios."

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THE BARIUM AZIDE PROCESS

Abel Santoro, LU8DXI

BRIEF HISTORY

In 1904, after hundreds of experiments, the German physicist Arthur Wehnelt found that a filament coated with an alkaline earth oxide is a copious low-temperature source of electrons. He devised a new technology to make cathodes of low temperature for radio tubes, based in the use of barium, calcium and strontium. Using these elements involved a paste which, appropriately diluted, was applied to the filament, giving a cathode with high electronic emission at low temperature. Thus was born the Whenelt or oxide-coated cathode, which could be heated directly or indirectly.

Around 1924, the Philips Laboratories in Eindhoven, Holland, in several subsequent experiments, discovered a new method to make directly heated oxide-coated cathodes of low-power consumption for radio tubes with better characteristics than previously known. The electron emission versus heating power thus achieved with this process, was better than that obtainable with thoriated tungsten or dull-emitter cathodes.

The research was directed to increase the electronic emission of the low temperature filaments of the type of oxides of alkaline earth metals, in this case specifically barium. Used commercially in Europe this was called the "Azide process," "Azide vapor process," "nitride process," or "distillation cathode." The most correct name would be "barium azide vapor process."

The barium azide process was introduced first to Britain in 1925 when Philips acquired half of the Mullard company, and later in France, when Philips purchased La Radiotechnique in 1931, although it is said that their tube factory already used this method in 1926.

Between 1924 and 1936 millions of radio tubes were made by this procedure.

PROCESS THEORY

Philips Laboratories discovered that the decay of a monatomic layer of barium, adsorbed on the surface of a metal wire as filament, due to evaporation, may be greatly delayed while the electronic emission of this layer will be greatly increased, simply interposing a monatomic layer of oxygen between the barium and the wire filament.

Fig. 1. Philips A 415

PREPARING THE BARIUM AZIDE

In chemistry, "azide" is the name given to the anion with the formula N_3^-. For the manufacture of cathodes under this method barium azide (BaN_6) was used, which, briefly, is prepared as follows: dry gaseous hydrazoic acid was made to react with barium carbonate in aqueous suspension; using acetone, the barium azide is precipitated by this reaction. The barium azide so formed is a chemical compound with colorless crystals, soluble in water, which begin to disassociate at 120°C and decomposes explosively when heated to 275°C. It is a chemical dangerous to use if not handled correctly because its dry

crystals are sensitive to shock, impact or friction.

PREPARATION OF A FILAMENT

The manufacture of a filament under the barium azide process may be divided into the following steps:

- Choice of the filament core.
- Oxidiation of the filament.
- Copper-coating of the filament.
- Coating of the copper plating with the barium azide.
- Processing of vacuum in the tube.

Tungsten, nickel or chromium nickel may be used as the filament core. Tungsten must be oxidized directly. For this the filament is heated in vacuum to about 1900°C to clean the surface, then cooled in an oxygen atmosphere a few seconds until it turns blue, thus forming an oxide layer on the tungsten.

Fig. 2. Philips B406

Another procedure is the copper-coating of the filament core by an electrochemical method. Once coppered, the filament is oxidized, heating it by an electric current in an oxidant atmosphere such air. The copper oxide is capable of alloying very well with barium metal.

The filament, thus prepared, is welded to the electrode supports, and to the inner surface of the anode is welded a small piece of fine nickel mesh on which is painted a solution of barium azide and alcohol. Tubes made this way are connected to the vacuum pumps and baked in an oven, drawing a vacuum in the tube. During baking the glass envelope of the tube is degassed while the plate is heated by an induction heater to decompose the barium azide into barium metal and nitrogen, the latter being absorbed by the pumps. Immediately the tube is tipped-off and the filament heated to about 850°C and a voltage of 50 volts is applied to the anode.

Now a green glow can be viewed inside the tube, which indicates the presence of barium vapor. It reacts with the tungsten oxide or with copper oxide on the filament, a layer of barium oxide is formed on the filament surface infused with barium metal. In this way the process is finished. The rest of the barium metal evaporated inside the tube condensed on the other electrodes and on the inner surface of the glass envelope, serving as a getter. Any other getter used in the tubes with barium azide cathodes was magnesium, which was evaporated immediately prior to decomposing the barium azide, yielding a mirrorlike silver appearance inside the bulb.

A filament made by this process exhibits a bright and clean metallic surface. Tubes with the barium azide process gave a life performance of thousands of hours.

A table of the manufacture of cathodes by the "Distillation method" or "Azide process" by Espe and Knoll [3] is as follows:

Preparation

Process: Distillation of barium metal on the cathode of radio tubes

Core of the cathode: Tungsten directly oxidized or tungsten coppered and then oxidized

Supply of Ba on anode: Barium azide (BaN_6)

Heating of the tube in an oven with the pump connected: Slowly to reach 180°C until no more N_2 evolving

Cathode heating: Slowly to reach 180°C until no more N_2 evolving. 10 minutes to 700-800°C

Degassing of the anode: not

Distillation

Cathode temperature: 700°C

Anode voltage: 0 V

Anode temperature by induction heating: Around 700°C

Removing the tube from the vacuum pump

Temperature to process the cathode: 1 hour under operating conditions (800°C

Some of the first Philips tubes made with this process were the following. All of these were directly heated.

Tube	Type	First series year	Filament: V @ mA
A106	Triode	1924	1-1.3 @ 60
A109	Triode	1925	1-1.3 @ 60
A209	Triode	1925	2 @ 80
A241	Tetrode	1925	1.7-2 @ 60
A404	Triode	1925	3.2-4 @ 60
A406	Triode	1925	3.2-4 @ 60
A409	Triode	1925	4 @ 65
A410	Triode	1924	4 @ 60

Tube	Type	First series year	Filament V @ mA
A430	Triode	1927	4 @ 60
A435	Triode	1927	4 @ 60
A441	Tetrode	1925	4 @ 80
B105	Triode	1925	1-1.3 @ 150
B403	Triode	1925	4 @ 150
B405	Triode	1926	4 @ 150
B406	Triode	1925	4 @100
B409	Triode	1925	4 @ 150
B424	Triode	1927	4 @100
B442	Tetrode	1928	4 @100
B443	Tetrode	1927	4 @ 150
B543	Pentode	1928	5 @ 100

Fig. 1 shows an A415 valve; Fig. 2 depicts a B406, while Fig. 3 shows a B424. In these valves can be seen the dark deposit on the inner surface of the bulb because of the azide process. It differs in color from the silver-mirror deposit produced by the barium getter.

Another tube made with the azide process was the PX4, from the Marconi Osram Valve Company of England in 1928. It was a higher-power version of the P410 which, too, was made with the barium vapor process.

The Philips-Mullard "PM" valves with the azide process were the PM3 and PM4. The PM3 was the first British-made azide type, from 1925. In 1928 was released to the market the Mullard valve PM12 which was coated with gold paint to disguise the blackening of the glass envelope from the azide process. This gold paint became characteristic of Mullard valves to 1938. Fig. 4 shows a Philips B442 valve with this coating.

Philips (Dario) Miniwatt B442

TROUBLES WITH THE PROCESS

In the tube manufacture, the barium azide process was not easy to control for several reasons. Because of the low temperature of decomposition of the barium azide (it begins to decompose at 120°C), the degassing of pipes and the envelopes of the tubes was difficult.

The heating process to decompose the material had to take place very slowly because otherwise the barium azide might explode inside the tube and the resulting pure barium be dispersed over all the electrodes and the glass walls of the tube. This heating process must be done by induction heating. This barium dispersed on the inner electrodes of the tube can cause short circuits and unstable operation of the tube. Barium azide must be stored damp with ethanol.

According to the amounts of barium azide used in each type of tube, at the time of decomposition by heat, large amounts of nitrogen (N_2), can be released, producing a sudden increase in the pressure in the tube. The pure barium metal taken in the process is only the 25% of the barium azide.

A typical feature of the barium azide method was the darkening of the internal walls of the glass envelope of the tube, giving an unsatisfactory appearance. Another problem of this method was the difficulty of depositing uniform layers of barium on the cathode.

Fig. 5. Horizontal mount.

Generally the electrode design of the tubes which used the barium azide process was built on a pinch with a horizontal electrode construction (Fig. 5), of the type with suspended supports by glass beads, for which the barium was not easily deposited between the electrodes forming short circuits with it, and unstable operation of the tube.

The barium azide is a product dangerous to use, if not handled correctly it can explode under certain conditions. This process was very expensive for the tube manufacturers to carry out.

The azide process was oriented mainly to the manufacture of tubes for battery radio receivers. When they stopped using batteries this process entered the end of its life which was prior to 1940.

The tube factories evolved to the production of tubes with indirectly heated cathodes using a coating of barium, strontium and calcium carbonates, which became the standard oxide coating in the modern tube industry.

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