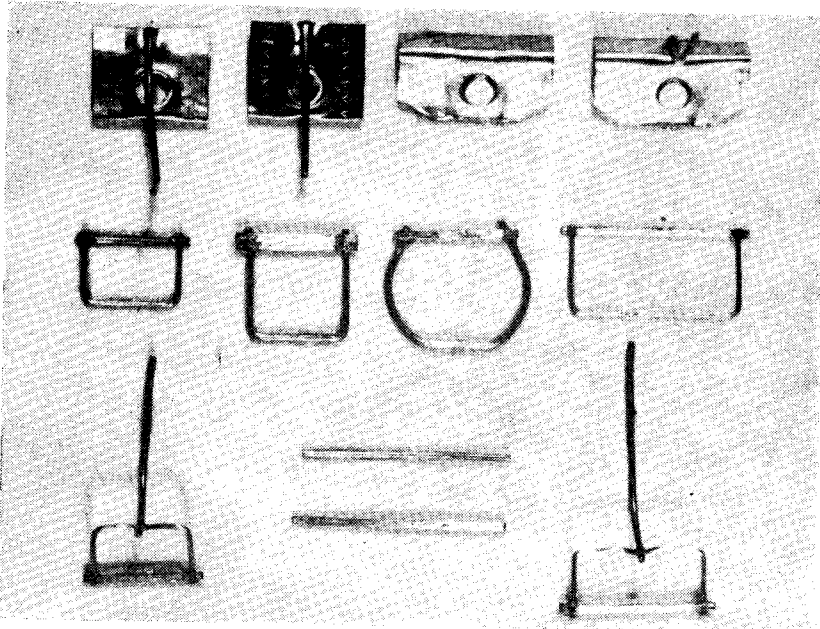


GETTER MATERIALS



Typical Ba flash getters for glass bulbs (upper row) and getter strip assemblies

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THE USE of getter materials is based on the ability of certain solids to collect free gases by adsorption, absorption or occlusion. This effect is widely utilized in the field of electronics to shorten the exhaust period and to improve and maintain a high vacuum or the purity of an atmosphere of noble gases.

Bulk getters are sheets or wires of gas-absorbing metals, which usually are heated for this purpose by mounting them on hot electrodes of the tube. In some cases the heating is accomplished by a separate heating source.

Coating getters are generally applied to those electrodes of vacuum tubes, which during service are maintained continuously at temperatures between 200 and 1,200 C. Such getters usually consist of non-volatile metal powders that are sin-

tered upon the electrode surfaces.

In the case of flash gettering, chemically active, comparatively volatile metals—mostly metals of the alkaline earth group—are evaporated by heating their supports at the conclusion of the pumping process. The metal vapor before and during condensation reacts instantaneously with all other than noble gaseous residues and forms on all cold parts of the tube, particularly on the tube walls, the so-called getter mirror. This surface, because of its large area, is capable of binding chemically or physically gases that are liberated during the life of the tube. With respect to the mechanism of gettering and the action of gases getter materials may be divided into two groups: corrosion type and solution type. From this aspect, barium (Ba) is the typical example

of chemical corrosion by gases and zirconium (Zr) an example of solution of gases in a metal. Corrosion takes place if the oxide film is porous and incoherent, thus not preventing further oxidation, which usually happens only if the volume of the oxide is smaller than that of the metal to be oxidized. In this case, the sorption of gas from the surrounding atmosphere can continue uninterruptedly. Oxides of the alkali and alkaline earth metals have less volume than the metal.

From a technical aspect the wide application of earth alkali metals for flashing getters in vacuum tubes is founded upon the fulfillment of the following requirements.

(1) During the standard degassing procedure at 400 C the getter should have low vapor pressure ($p < 10^{-2}$ mm Hg).

(2) The getter should be readily vaporized at its activation temperature. This temperature range must be high enough so that the getter may be readily degassed prior to the flashing; on the other hand, it must be sufficiently low to avoid the evaporating, melting or loosening of electrode metals. For nickel supports this establishes a temperature range of 600 to 1,000 C.

(3) After flashing, the getter deposit on the tube glass wall must have a negligibly low vapor pressure ($p < 10^{-7}$ mm Hg) assuming the operating temperature of the vacuum tube at 200 C.

(4) Between ambient and operating temperature the getter should be very active for all gases, especially oxygen. The oxide film created must be porous and incoherent in order that the gases may diffuse without hindrance into the interior of the getter mirror and may be absorbed also by getter molecules in the volume of the getter material.

for ELECTRON TUBES

The specific action and applicability of Ta, Cb, Zr, Th, Ti, Al, Mg, Ba and P as getters for vacuum tubes are shown. They can be formed as wires, sheets, tubes and tablets directly or indirectly heated; they may be powder coatings on hot electrodes; or they can be flashed

(5) The chemical compounds should be stable in order that during operating temperature or electron bombardment the absorbed gases are not expelled. For gas-filled tubes, the absorbed residual gas should not be replaced during operation by the filling gas, for example—Hg-vapor in tubes.

The first requirement is satisfied by all earth alkali metals. As seen from Fig. 1, Mg is near the border line, and cannot be used in tubes with high operating temperature because of the danger of migration of Mg atoms. Requirement 2 is met by all earth alkali metals but not by aluminum. Requirement 3 is met by all earth alkali metals with the exception of magnesium. The fourth requirement, with emphasis on activity, is met by all earth alkali metals with the exception of magnesium and aluminum. In a similar manner requirement of an incoherent oxide layer is not met by magnesium and aluminum. Requirement 5 (stable reactions) is met by all earth alkali metals but only up to a temperature of 200 C (regarding the oxides created even up to higher temperatures).

The materials Sr, Ba and Ca, are the most suitable for flash getters in high-vacuum electron tubes. Concerning the replacement of absorbed gases by mercury vapor, however, all earth alkali metals fail with the exception of magnesium, which is the reason that the latter metal is used in mercury tubes.

There are few quantitative data that permit a comparison of the getter-efficiency of different metals for different gases. Table I shows such a comparison for flashed deposits of Al, Mg, Th, U, mischmetal and Ba and the gases O₂, H₂, N₂, and CO₂. It exhibits Ba as the

most efficient getter among the metals investigated. The higher efficiency of diffuse deposits is due to their much larger surface, resulting from their finely divided state. This phenomenon, known as dispersal gettering is illustrated by the black Ba deposit.

The practical choice of the proper getter material is a function of factors other than efficiency alone. The broad use of high-efficiency flash getters requires considerations of insulation, interelectrode capacitance, contact potential and secondary emission of vacuum-tube electrodes and insulators, which often suggest their avoidance. On the other hand, Ba flash getters are preferred for oxide-coated cathodes because the Ba does not poison the cathodes and in some cases will improve the BaO cathodes. Judicious use of shields and proper positioning of the flash getters

avoids most of their disadvantages.

It has been known for a long time that almost all metals (after thorough degassing) are capable of adsorbing gases on their surfaces.

Tantalum

Certain metals are capable of incorporating gases, even noble gases, by solution in their bulk volume. The classical example is tantalum which, on account of this property, plays a predominant role in the construction of high-power transmitting tubes. After degassing in a high vacuum for several hours at a temperature of 1,600 to 2,000 C, tantalum is capable of absorbing gases in amounts up to several hundred times its own volume. The optimum gettering temperature for tantalum appears to be in the neighborhood of 1,000 C. At temperatures above 1,500 C, the gettering action is reversed. The maximum getter effect is secured, therefore, by dimensioning tantalum anodes so that during normal service the electrodes operate at red to yellow heat. Generally, the high price of tantalum sheets and wires limits the use of whole tantalum electrodes to particularly valuable tubes and suggests the coating of electrodes with tantalum powder. This is mostly performed by applying very fine tantalum powder on the surface of anode sheets in the finished assemblies. They are sintered together while simultaneously degassing these powders during the pumping operation by means of high-frequency heating or by electron bombardment. On account of the high degassing temperature required for tantalum, only molybdenum or tungsten is suitable as a base metal for tantalum powder. Tantalum should never be hydrogen-fired because of embrittlement

Table I—Comparison of Getter Efficiency for Metals and Gases

Getter	Gas	Efficiency (in microns of pressure)	
		Bright deposit	Diffuse deposit
Al	O ₂	7.5	38.6
	N ₂ , H ₂ , CO ₂	—	—
Mg	O ₂	20	202
	CO ₂ , N ₂ , H ₂	—	—
Th	O ₂	7.45	31.15
	H ₂	19.45	53.7
U	O ₂	10.56	9.26
	H ₂	8.9	21.5
Mischmetal	O ₂	21.2	50.9
	H ₂	46.1	63.9
	N ₂	3.18	16.1
	CO ₂	2.2	44.8
Ba	O ₂	15.2	45
	H ₂	87.2	73
	N ₂	9.5	36.1
	CO ₂	5.21	59.5

Getter efficiency is determined by the product of volume (1 liter) and pressure of gas cleaned up by 1 mg getter material. Diffuse deposits were obtained by flashing the getter in argon and consist of finely divided getter material.

and consequent destruction by this gas.

The main disadvantages of tantalum are the high material cost and the high temperature range required for proper degassing and subsequent gettering operation.

Columbium

During recent years columbium getter pellets have been introduced to the vacuum technique. These pellets are approximately three to five millimeters in diameter and one to three millimeters high, and consist of oxide-free columbium metal.

The getter pellets must occupy a position in the tube where they can be heated to a high temperature during exhaust by either high-frequency induction or electron bombardment. The position of the pellet must be such that the temperature is maintained by either radiation or electron bombardment at approximately 500 C. This temperature is not critical but must be above 400 and less than 900 C. A temperature of 1,650 C is needed to outgas columbium pellets because at this temperature occluded and absorbed gases are expelled and columbium oxide is volatilized. A temperature lower than 1,650 C will not accomplish this expulsion of columbium oxide. The outgassing time may vary from a period of five minutes to a somewhat longer time. The preferred manner for supporting the columbium getter pellet is to weld a molybdenum wire to it. The temperature of out-

gassing is too high for a nickel support but is in the proper range for molybdenum. Tungsten need not be used.

Zirconium

Zirconium has valuable gettering characteristics and has come into wide use during the past decade. It forms very stable solid solutions (or compounds) with such gases as O, N, CO and CO₂. Zirconium metal is cheaper than tantalum and requires somewhat lower operating temperatures. Zirconium is available either in solid metal form (sheets or wires) or it may be applied in the form of a powder to base metals (molybdenum) as described above. The proper outgassing temperature for zirconium lies between 1,000 and 1,700 C, which is attained by either direct or indirect heating of the zirconium metal or of the base metal to which zirconium metal or zirconium powder has been applied. Wherever it is deemed inadvisable to heat the getter material to this temperature range, an outgassing temperature of 700 C must be considered minimum for activating the surface of the zirconium getter. While zirconium is effective as a getter from about 400 C on, it is most active at temperatures up to 1,600 C if used, for example, on molybdenum and carbon anodes.

The solubility of H₂ in Zr at room temperature equals 1,500 times its own volume at 1 atmosphere. Sorp-

tion begins at 300 to 400 C and is completed at 500 C. As the temperature is increased, the metal frees H₂, but at 850 C the H₂ is again taken up during transition from α to β Zr. Above 850 C, H₂ is evolved. Sorption and desorption are reversible with decrease in temperature. Preliminary heating to a high temperature is a necessary condition for the sorption of H₂ at lower temperatures. During a rapid passage from a high temperature (above 1,200 C) to room temperature, a large amount of H₂ is quickly taken up.

Oxygen as well as N₂ dissolve homogeneously in Zr. When a Zr rod covered with a thick white oxide layer is heated in vacuum, the metallic luster reappears. Water vapor is cleaned up between 200 to 250 C. Care must be taken that a part of the Zr getter remains at a low temperature (approximately 400 C) during operation in order to bind the H₂, while another part must assume much higher temperatures (approximately 800 C) in order to absorb O₂, N₂ and other gases.

Zirconium metal in sheet form 0.002 to 0.005 inch thick is used on locations that can be properly outgassed and which operate in the temperature range indicated above. Very often zirconium sheets are mounted to grid shields, cathode supports, and other structures, which during operation attain a temperature of 600 to 800 C. In small tubes zirconium sheets, cylinders, or ribbons are used for cathode supports, grid supports and radiation shields. Zirconium wire of 0.005 to 0.020-inch diameter can be mounted for direct heating, being heated whenever absorption of gas is required, or it may be mounted for the same purpose by winding zirconium wire around Mo rods or other suitable structures.

Continuous gas absorbers such as that shown in Fig. 2 provide a support for the Zr wire and are operated from 350 to 1,700 C, for example, in x-ray tubes in series or in parallel with the filament (the temperature being adjusted by proper length of the wire). They have also been used for shortening the degassing time of electrode systems during pumping. Using a

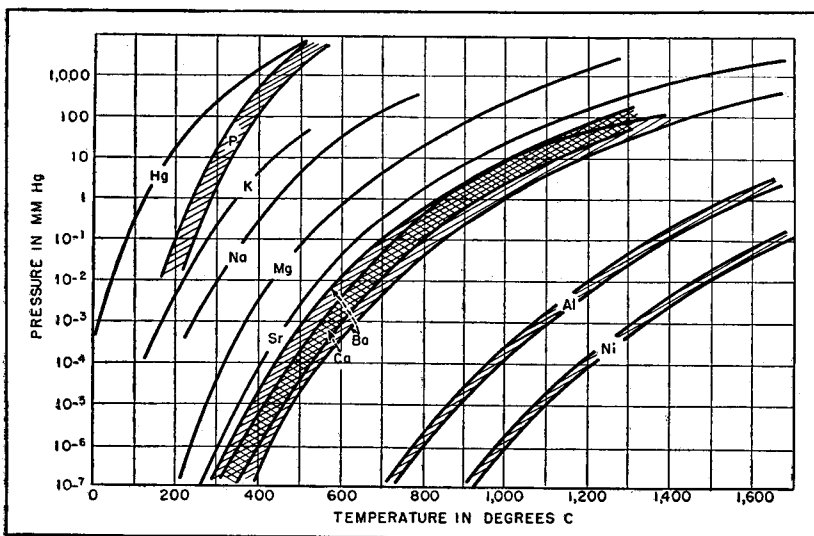


FIG. 1—Vapor pressure of metals used as flashing-type getters. Hg and Ni are included for comparison

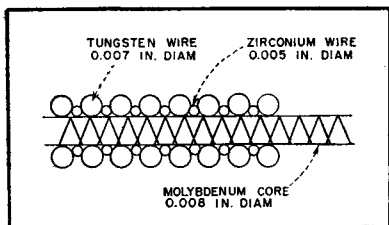


FIG. 2—Zirconium-wire assembly for continuously heated gas absorber

Zr wire spiral of fifteen turns on a 0.040-inch Mo mandrel, treated and outgassed for one hour at 1,700 C, a pressure of 5×10^{-6} mm Hg was reached in ten minutes instead of thirty minutes with the high vacuum pump alone. This auxiliary pumping getter can be used repeatedly even though exposed to atmospheric pressure between pumping cycles, no additional outgassing between cycles being required. In every case the Zr absorber maintained a higher vacuum at a considerably higher effective pumping speed than the 20-liter-per-second high-vacuum pump.

A convenient way of using zirconium is to spray the tube parts with fine zirconium powder. Such powders, of particle size between 1 and 8 microns, may be suspended in a temporary binder such as nitrocellulose dissolved in amyl acetate. For high voltage tubes a permanent binder such as colloidal silicic acid has been used with success. Such a binder has the further advantage of not giving off gaseous products during outgassing and operation. The amount of binder is usually two to five percent. This mixture is sprayed on the electrode parts, which in turn are fired in vacuum in order to remove the binder or to convert the binder to a stable compound. Nickel electrodes (preheated at 1,000 C, operating at 200 to 500 C), molybdenum electrodes (preheated at 1,300 C in vacuum and operating at 800 C) and graphite electrodes can be satisfactorily coated with such mixtures. Quantitative data on the sorption of different gases at different temperatures by powdered Zr are shown in Table II. Other methods of applying zirconium powder to electrodes have been reported, such as a suspension mixture consisting of paraffin, naphthalene, xylene and methanol or deposition of zirconium

powder by cataphoresis.

Zirconium hydride (ZrH_2) may also be applied to Mo, Ni, Fe or graphite anodes or grids as a paste, by spraying or cataphoretic precipitation, and reduced to pure Zr upon heating. This compound compared with pure Zr powder presents the advantage that at lower temperatures the zirconium is tied up and protected against oxidation or poisoning during seal-in and exhaust. Then as the temperature is raised, metallic zirconium is formed, liberating its hydrogen completely in vacuum at about 800 C. Thus, for coating on carbonized plates, which liberate much adsorbed gas during exhaust, zirconium hydride may be preferable to the pure metal since not only is the combined zirconium protected from the evolved gases but furthermore the hydrogen that it liberates at higher temperatures apparently reduces the last traces of adsorbed oxygen in the carbon layer.

Zirconium has been used successfully in high-power transmitting tubes, especially tubes having thoriated tungsten filaments, small microwave tubes and gaseous discharge tubes. Zirconium is inert to mercury vapor.

Stable solutions or compounds of Zr are formed with most gases including water vapor, with the exception of hydrogen.

The chief disadvantage of zirconium as a getter is that the optimum temperature for the sorption of hydrogen is too low for the effective cleanup of oxygen, nitrogen and the oxides of carbon. If, therefore, the zirconium-coated part is to operate at a temperature much in excess of 300 C, a supplementary lower temperature Zr getter or a getter of the barium or barium-magnesium type should be added to absorb the hydrogen. Whether this precaution is necessary or not depends upon the tube and the amount of water vapor or pure hydrogen found within it.

Thorium

During World War II, thorium, thorium alloys and mixtures of these with other getter materials were developed in Germany for use in vacuum tubes. Thorium metal is manufactured by reduction of ThO_2

with Ca. Powdered Th is very pyrophoric; it is inflammable by mere friction. Electrode parts were coated with thorium powder by cataphoresis and heated for two to three hours in a vacuum furnace. For wires the coating was 5 to 10 microns thick and for sheets 1 to 2.5 mg per sq cm. The heating temperature is about 800 to 1,000 C for nickel and iron and 1,500 to 1,600 C for graphite electrodes. Considerable gas absorption is reported to occur around 200 C but especially in the range from 400 to 500 C. This getter is therefore suitable for power tubes and very small tubes with high anode temperatures. If the anode is covered with thorium powder its surface finish is rough, resulting in increased emissivity by blackening.

One alloy of thorium is the getter called Ceto, which comprises a 20-percent mischmetal, (chiefly cerium) and 80 percent thorium. This powder mixture is sintered at approximately 1,000 C, and the bars are milled to powder again. It is very inflammable. Ceto getter powder is transformed with amyl acetate into a paste that is applied to the tube electrodes in the amount of 15 to 25 mg powder per sq cm and then sintered upon the base metal in a vacuum furnace. The degassing temperature of the Ceto getter is 800 C and a marked getter action is exhibited from 80 to 130 C up, with an absorption maximum at 200 to 500 C.

Ceto getter material has a lower secondary emission than barium. It is used when it is desired to avoid or to reduce secondary emis-

Table II—Sorption of Gases by Powdered Zirconium

Gas	Temp C	Gas sorbed (cu cm \times mm Hg per mg Zr)
O ₂	25	0.38
	400	1.99
N ₂	500	0.11-1.0
	800	1.46
CO	25	0
	500	0.43
	800	3.65
CO ₂	25	0
	500	0.57
	800	3.04
H ₂	25	0.09
	350	13.33

sion that might arise from the use of Ba. It cannot be used above 600 C. Ceto bridges the gap between the low-temperature flashing getter such as Ba and the high-temperature non-volatile types (Th, Ta and Zr.) Pure thorium or compounds of Th and Zr are highly pyrophoric.

Titanium

A recent addition to bulk getter materials is titanium, which can be used either as bulk or as coating getter. It is not pyrophoric and its getter properties are good, besides being easy to form and machine. Blackening of the parts can be obtained by a short heating in air. At present titanium sheet is more expensive than zirconium per unit of gas absorbed.

Aluminum

Aluminum in its pure state is not used as a flash-getter, chiefly because its vapor pressure is too low (see Fig. 1). It vaporizes sufficiently only above 1,300 C, which is much too high for the conventional base metals like Ni. On the other hand, aluminum plated on Fe to a thickness of about 15 microns shows a considerable coating-getter effect for traces of O₂ being bound by the carbon content of Fe electrodes and released only slowly during the life of the tube. After heating at 700 to 800 C in vacuum, the aluminum forms a black compound with the Fe base (FeAl₃ or FeAl₅). This blackening increases the total emissivity to a level that is equal to or greater than that of carbonized Ni anodes. Such Al-plated sheet-iron has been widely used in Europe for anodes in receiving and amplifier tubes with oxide-coated cathodes.

The trade name for sheet iron plated with aluminum on both sides is P2-iron; plated with Al on one side and with Ni on the other—PN-iron.

Magnesium

Pure magnesium possesses many desirable properties for a getter material, such as availability in suitable forms, and being comparatively stable and volatile under vacuum at convenient temperatures around 500 C. Unfortunately, the gettering power of magnesium is

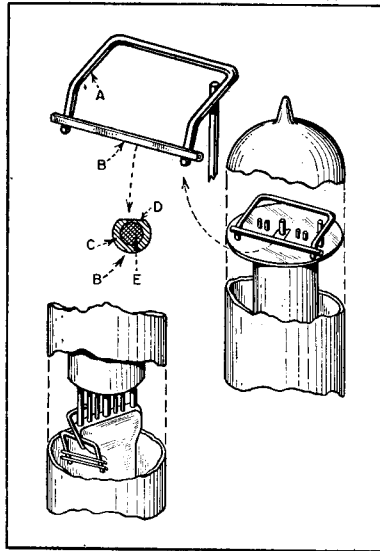


FIG. 3—Typical Kemet KIC getter mountings; A is nickel h-f induction loop, B getter strip, C iron sheath, D weakened zone to allow evaporation and E is 0.5 to 25-mg barium filling

not high because most gases are only physically absorbed. As a result, magnesium by itself is not used in high-vacuum tubes. The only evidence of its use is in Hg-vapor-filled rectifiers and in certain types as a grid coating powder to reduce secondary emission.

In order to obtain a material of greater stability and safety in use than pure magnesium, the so-called Formier getter was developed. It consists of aluminum-magnesium alloy powder (55 percent Al, 45 percent Mg) which is applied suspended in a nitrocellulose binder and applied to tube parts as a paint. On account of the limited gettering powers of magnesium, Formier is used only when other types of getters with higher evaporation temperatures must be avoided. Magnesium getters are difficult to degas, have little gas absorption up to temperatures of 175 C and absorb only oxygen. High vapor pressure precludes use in small tubes and at high operating temperatures.

Barium

The active ingredient of most flash getters is barium, which is used in combination with aluminum, magnesium, tantalum, thorium, strontium or calcium. The getter is attached to the electrodes in the form of a pellet, or more frequently, to a special metallic support within the tube as shown in

the top row of the accompanying photograph. It is mounted in such positions as to insure that the vapor stream produced is not splashed against such parts as the stem or the insulated lead-in wires. Shielding screens of metal, mica or ceramic materials are often provided to prevent this. The getter pellet must be attached to parts that during the pumping process may be readily heated to the evaporation temperature of the getter. This heating is performed by electron bombardment or, more frequently, by high-frequency induction from coils arranged outside the tube.

Flash getters of pure barium have the disadvantage that the unprotected barium reacts at room temperature with oxygen or with water vapor, thereby becoming inactive. This condition may be prevented by using: a protective layer or casing, alloys of Ba that are inert at room temperature or by generating the gettering material in the vacuum tube by a chemical reaction between stable Ba compounds and deoxidizing agents to form a reaction-type getter. Alloys of barium with magnesium and aluminum are relatively stable at room temperature and yield pure barium upon dispersal or flashing of the getter. The percentage of metals in standard alloys for getter tablets are: Ba 25, Mg 55, Al 20; Ba 37, Mg 37, Al 26; Ba 43, Mg 20, Al 37 (known by the trade name Kemet). The tablets are mounted on nickel flags of various shapes.

Barium-magnesium alloys yield very little Ba metal in the flashing and are, therefore, seldom used in modern high-vacuum tubes. Ba-Al getters provide much larger amounts of Ba metal, which accounts for their wider use. A common disadvantage of both types of alloys is their rapid rate of deterioration upon exposure to air and the necessity of vacuum packing.

Another commercial assembly is shown in Fig. 3. Other types comprise short pieces of iron, nickel and copper-clad barium wires to be mounted on a support of Ni-sheet, which can be high-frequency flashed at 900 to 1,100 C. Trade names of these materials are Feba, Niba and Cuba.

Several x-ray tubes of European

make use iron-clad barium (Feba) getter made in wire form, 2 mm diameter by 15 mm long. The getter is mounted within a miniature oven consisting of a ceramic tube into which the getter just fits. A tungsten spiral heater is wound on the outside of the ceramic tube. Care must be taken to avoid the possibility of migration of the barium to active tube elements. After sealing off the tube, the getter is flashed by heating the spiral.

Examples of the reaction type Ba getters are the reduction of BaO by Al to Ba (Alba getter) and of BaCO₃ or barium beryllate by Ta to Ba. In the case of BaCO₃, a tantalum wire heater is coated with a mixture of BaCO₃ and SrCO₃ (SrCO₃ prevents fusing of BaCO₃). At 800 to 1,100 C the carbonates dissociate to oxides and at 1,300 C the oxides react with Ta to form metallic Ba, whereby 40 percent of the theoretical Ba yield is obtained in the so-called Batalum process. Also barium beryllate (BaBeO₂) is stable in air and is used in a directly heated getter, shown in Fig. 4, formed in the shape of a trough from a 0.040 × 0.001 in. Ta ribbon, which holds approximately 2.5 mg of Ba and gives a Ba yield of 60 percent.

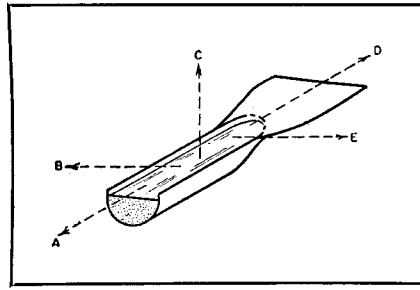


FIG. 4—Arrows indicate direction of barium metal evaporation from barium beryllate in tantalum trough

Another flashing-reaction-type getter is the so-called Bato getter, which is prepared by mixing an aluminum-barium alloy with iron oxide and thorium powder. Its purpose is to provide a source of heat in the getter pellet and in so doing aims at flashing Ba metal at a relatively low getter flag temperature. The source for the Ba is the Ba-Al alloy and the latent heat so derived forms an exothermic reaction between iron oxide and metallic thorium. The powder is formed into tablets, which are pressed into nickel cups and attached to special supporting members within the tube. Since it is important to store the Bato getter in a dry atmosphere, the getter flags are usually sealed into evacu-

ated ampoules or cans. After the pumping process, the getter is evaporated by high-frequency.

Flash getters are outgassed at temperatures between 600 and 700 C, usually by r-f heating from the outside of the tube, and flashed at temperatures between 900 and 1,300 C. The barium vapor condenses on the cold surface opposite the getter material, usually on the envelope of the tube. The appearance of the condensed getter deposit depends upon the vapor pressure in the tube at the time of flashing. If the getter is vaporized very slowly, the first barium atoms evaporated will absorb the gas present so that the remaining getter is deposited in a very high vacuum, exhibiting a shining mirror. If flashing is done very rapidly, however, the getter deposits in a rather high vapor pressure and the getter mirror will be discolored due to dispersion of the Ba. If vaporization is carried out in the inert atmosphere of a rare gas the condensed deposit will be black, resulting in a dispersal getter. This condition does not mean that the getter is contaminated, but merely that the deposit is finely divided and therefore absorbs light. Such deposits exhibit higher efficiency than the

Table III—Outgassing, Flashing and Operating Temperatures of Typical Getters

Material	Ta	Cb	Zr	Th	Ceto	Ba And Ba Compounds			Reaction-Type Getters			Phosphorus
						Mg	Al-Mg	Bato	Batalum	Ba-Beryllate		
Form of Application	bulk coating	bulk	bulk coating	coating	coating	flash	flash	flash	flash	flash	flash	flash
Form of Getter	sheet powder	pellets	sheet wire powder	powder	powder	ribbon wire	powder paint	metal-clad wire pellets	Ni-clad pellets	BaCO ₃ paint on Ta	BaBeO ₂ paint on Ta	powder suspension
Outgassing Preheating Temperature (deg C).	1,600-2,000	1,650	700-1,300 (up to 1,700 in compound wires)	for metal base 300-1,000 for graphite wires 1,500-1,600	800-1,200	400	400	600-700	no ref	800-1,100	900-1,000	no ref
Flashing Temperature (deg C).	—	—	—	—	—	500	no ref	900-1,300	750-800 (900)	1,200-1,300	1,300	>200
Operating Temperature (deg C).	700-1,200	500	800 (up to 1,600 in compound wires)	400-500	200-500	absorbs gases only during flashing	20-200 max	20-200	20-200	20-200	20-200	100-200
Applications Reported	D, E, M	D, E	C, D, E, F, I, K, L, M, N	C, D	P	I, K	A, F	A, B, D, F, G, H, I, (L), N	D, M	A, F	A, F	O

A — Small receiving tubes	G — Cathode-ray tubes	N — Tubes with thoriated cathodes
B — Miniature tubes	H — Phototubes	O — Incandescent lamps
C — UHF tubes	I — Gaseous-discharge tubes	P — Vacuum tubes in which neither flashing getters nor the high temperatures necessary for Ta and Zr may be used
D — Medium-size transmitting tubes	K — Hg-vapor tubes	
E — High-power transmitting tubes	L — X-ray tubes	
F — Oxide-cathode tubes	M — High-power vacuum tubes	

bright deposits indicated in Table I.

Barium reacts with atmospheric gases such as oxygen, nitrogen and carbon dioxide at room temperature, as well as with hydrogen and carbon monoxide. This absorption at low temperature makes flash getters particularly valuable for tubes that do not attain high operating temperatures. If the volume of the vacuum tube is large, multiple getter strips or several getter pellets are employed.

Flash getters have the disadvantage that during flashing metallic vapor is produced, which may settle on insulating parts or build up a conducting layer on the glass envelope. Such layers may become charged during operation or represent interelectrode capacitance. Usually flash getters are inadvisable in high voltage tubes or in microwave tubes, the latter type having very close spacing and only short insulating surfaces. It should also be considered that the opaque mirror interferes with the cooling of electrodes by radiation. In high-voltage types like transmitting and x-ray tubes fast stray electrons may hit the mirror and evaporate sufficient getter material to cause a gas discharge followed by a short circuit and destruction of the tube.

Phosphorus

Phosphorus has a comparatively high vapor pressure (indicated in Fig. 1) and for this reason it is not used in radio transmitting, x-ray, or other high-vacuum discharge tubes. Inexpensive and simple to handle, it is used for high-vacuum and gas-filled lamps, especially for types of below 60 watts with voltages of 90 to 250 volts.

The outgassing, flashing and operating temperatures of typical phosphorus getters are given in Table III.

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BIBLIOGRAPHY

Condensed Papers and Books

- S. Brunauer, "The Sorption of Gases and Vapors", Princeton 1942.
J. DeMent and H. C. Duke, "Rarer Metals", New York 1946.
S. Dushman, "Scientific Foundations of

Vacuum Technique", John Wiley and Sons, New York 1949.

W. Espe, New Getter Materials for the High Vacuum Technique, *Powder Metallurgy Bulletin*, p 100, Oct. 1948.

W. Espe and M. Knoll, "Materials of High Vacuum Technique", p 305, Ann Arbor 1944 (in German).

Faraday Society, London, "The Adsorption of Gases by Solids", p 447, Oxford 1932.

J. D. Fast, Metals as Getters, *Philips Tech. Rev.*, 5, p 217, 1940.

S. I. Gregg, "Adsorption of Gases by Solids", p 116, London 1934.

D. B. Langmuir and L. Malter, The Rate of Evaporation of Ta, *Phys. Rev.* 55, p 748, 1939.

M. Littmann, "Getterstoffe", Leipzig 1938.

I. W. McBain, "The Sorption of Gases and Vapours by Solids", London 1932.

A. E. Van Arkel, "Reine Metalle, Herstellung, Eigenschaften, Verwendung", Berlin 1939.

Gettering and Getters, *Light Metals*, p 34, Jan. 1944 and p 77, Feb. 1944.

J. S. Harrison, Production and Use of Getters and Materials in German Radio Valves, Thermionic Devices and Electric Lamps, B. I. O. S., Final Report No. 1834, London 1948.

Gettering by Evaporated Metals and Alloys

G. Ahrens, Cerium, *Mod. Metals*, p 20, Sept. 1945.

M. R. Andrews and J. S. Bacon, The Comparison of Certain Commercial Getters, *J. Am. Chem. Soc.*, 53, p 1674, 1931.

M. Benjamin, C. W. Cosgrove and G. W. Warren, Modern Receiving Valves; Design and Manufacture, *J. Inst. El. Eng.*, 80, p 421, 1937.

J. E. DeGraff and H. C. Hamaker, The Sorption of Gases by Ba, *Physics*, 9, p 297, 1942.

S. Dushman, Recent Advances in the Production and Measurement of High Vacua, *Journ. Frank. Inst.*, 211, p 689, 1931.

L. F. Ehrke and C. M. Slack, An Investigation into the Gettering Powers of Various Metals for the Gases H₂, O₂, Na₂ CO₂ and Air, *Journ. Appl. Phys.*, 11, p 129, Feb. 1940.

G. Haase, Die Getterwirkung duenner Ba Filme bei tiefen Drucken, *Zeit. f. ang. Physik*, 2, p 188, 1950.

G. L. Hunt, Telefunken Metal Ceramic Radio Valves, B. I. O. S. Final Report 30, London 1945 (Dept. of Commerce, P. B. 18901).

G. W. Johnson, W. H. Hane and P. A. Anderson, A Quantitative Study of the Clean Up of H₂ by Ba, *Phys. Rev.*, 56, p 852A, 1939.

Getters and Gettering Methods for Electronic Tubes, Kemet Labs., 1947.

E. A. Lederer and C. H. Wamsley, Batulum, a Ba Getter for Metal Tubes, *RCA Review*, p 117, 1937.

E. A. Lederer and C. H. Wamsley, Recent Advances in Ba Getter Technique, *RCA Review*, p 310, Jan. 1940.

A. L. Reimann, The Clean Up of Various Gases by Mg, Ca and Ba, *Phil. Mag.*, 16, p 673, 1933 and 18, p 1,117, 1934.

N. W. Robinson, Rugged Valves and Mechanical Tests for Valves and Components, B. I. O. S. Final Report 501, London 1945.

C. C. Van Voorhis, A. G. Shenstone and A. W. Pike, Purification of Inert Gas with Mischmetal, *Rev. Sci. Inst.*, 5, p 367, 1934.

R. Wild, Les Getters et leur Emplois, *LeVide*, 2, p 252, 1947.

Gettering by Solid Metals and Alloys

C. I. Bradford, J. P. Catlin and E. L. Wemple, Properties of Wrought Commercially Pure Titanium Prepared by Arc Melting and Casting, *Metal Progress*, 55, p 348, 1949.

I. E. Campbell and others, The Preparation and Properties of Pure Ti, *Journ. Electrochem. Soc.*, 93, p 271, 1948.

W. Daellenbach, Grossgleichrichter ohne Vakuumpumpe, *Elektrotechnische Zeitschrift*, 55, p 85, 1934.

R. S. Dean, and B. Silkes, Metallic Titanium and Its Alloys, U. S. Dept. Int., Bur. of Mines Information Circular 7381, p 38, Nov. 1946.

I. H. DeBoer and J. D. Fast, The α - β Transition in Zr in the Presence of H₂, *Rec. Trav. Chim.*, 55, p 350 and P 459, 1936.

I. H. DeBoer and J. D. Fast, Electrolysis of Solid Solutions of Oxygen in Metallic Zr, *Rec. Trav. Chim.*, 59, p 161, 1940.

I. H. DeBoer and J. D. Fast, Zr: I; *Z. An. Chemie*, 153, p 1, 1926 and 187, p 177, 1930.

W. Deck, The Adsorption of Gases by

Steel Walls of a Vacuum Discharge Apparatus and Its Bearing on the Life of Pumpless Mutators, *BBC Review*, 29, p 202, Aug. 1942.

E. I. du Pont de Nemours, Inc., Titanium Metal, *ELECTRONICS*, 2, p 207, March 1949.

W. Espe, Platovane zelezo jako nový materiál vakuové techniky, *Slaboproudý Obzor*, 11, No. 2, p 31, 1950.

W. Espe, Metalické Thorium, nový zajímavý materiál techniky vakua, *Slaboproudý Obzor*, 11, No. 5, 1950.

W. Espe and V. Kratochvíl, Titan-kov blitžke budoucnosti, *Slaboproudý Obzor*, 11, 1950.

G. A. Espersen, Zr for Electron Tubes, *Footprints*, 18, No. 1, p 3, 1946.

Fansteel Metallurgical Corp., Information for Use of Columbian Getter Pellets, Chicago.

Fansteel Metallurgical Corp., Columbian; Technical Information, Chicago 1946.

Fansteel Metallurgical Corp., Tantalum; Technical Information, Data Bulletin Ta 500, Chicago.

J. D. Fast, Ductile Shaping of Zirconium and Titanium, *Metalwiss.*, 17, p 459, 1938.

J. D. Fast, Zirconium, *Footprints* on Chemicals, metals, alloys and ores, 10, p 1, Dec. 1937 and 13, p 22, 1940.

J. D. Fast, Zirconium and Its Compounds with a High Melting Point, *Philips Tech. Rev.*, 3, p 345, 1938.

H. W. Gillet, Some Features of Ductile Zirconium and Titanium, *Footprints*, 13, p 1, 1940.

A. Greenwood, Titanium, Some Properties and Applications, *Metallurgia*, 36, No. 211, 1947.

W. G. Guldner and L. A. Wooten, Reactions of Zr with Gases at Low Pressure, *Journ. Electrochem. Soc.*, 93, p 223, 1948.

S. Hukagawa and J. Nambo, Absorption Properties of Metallic Zr and its Application to Electron Tubes, *Electrotech. Journ.* (Japan) 5, p 27, 1941.

W. J. Kroll and A. W. Schlechten, Survey of Literature on the Metallurgy of Zr, Bureau of Mines Information Circular No. 7341, 1946.

W. J. Kroll and A. W. Schlechten, Titanium and Zirconium—Two Metals of the Future, *Metal Industry*, 69, p 319, 1946.

O. Kubaschewski, Die Löslichkeit von Gasen in Metallen, *Zeit. f. Elektrochemie*, 44, p 152, 1938.

W. C. Lillendahl and others, The Quantitative Evaluation of O₂ in Zr, *Journ. Electrochem. Soc.*, 93, p 235, 1948.

J. R. Long, The Consolidation of Titanium Powder by Sheath Rolling, *Metal Progress*, 55, p 191, 1949.

J. W. Marden and M. N. Rich, Investigations of Zirconium, *Ind. Eng. Chem.*, 12, No. 7, p 651, 1920 and Bureau of Mines Bulletin 186, Mineral Technology 25, 1921.

W. C. Michels and S. Wilford, The Physical Properties of Titanium, *Journ. Appl. Phys.*, 20, p 1,223, 1949.

A. L. Reimann and C. K. Granz, Some High Temperature Properties of Niobium, *Phil. Mag.* p 34, 1936.

E. R. Owen, Telefunken Special Materials for Radio Valves, B. I. O. S. Final Report 276, London 1945 (Dept. of Commerce, P. B. 27121).

M. Pirani, Ta und H₂, *Zeit. f. Elektrochemie*, 11, p 555, 1905.

O. C. Ralston, and F. J. Cservenyik, Potential Uses of Titanium Metal, *Ind. Eng. Chem.*, 42, p 214, 1950.

A. N. Rogers, Use of Zr in the Vacuum Tube, *Trans. Electrochem. Soc.* 88, p 207, 1945.

O. W. Simmons and others, Arc Melting of Titanium, *Metal Progress*, 55, p 197, 1949.

I. B. Sutton and T. D. McKinley, Induction Melting of Titanium in Graphite, *Metal Progress*, 55, p 195, 1949.

E. Wainer, Technology of Zr and Ti and their Compounds, *Ceramic Age*, 48, p 198, Nov. 1946.

F. S. Wartmann, Production of Titanium Powder by the Bureau of Mines, *Metal Progress*, 55, p 188, 1949.

E. Wedekind, Ueber die Darstellung des sog. kristallisierten Zr im el. Ofen, *Zeit. f. Elektrochemie*, 10, p 331, 1904.

L. V. Whitney, Temperature Scale of Cb, Th, Rh, Mo at 0.667 μ , *Phys. Rev.*, 48, p 458, 1935.

Gettering by Phosphorus

W. J. Bartlett, Chemistry in Incandescent Lamp Manufacture, *Ind. Eng. Chem.*, 21, p 970, 1929.

S. Dushman, Methods of Production and Measurement of High Vacua, Part IX, Physical Chemical Methods, *G. E. Rev.*, 24, p 669, 1921.