

# The Bulletin of the BISMUTH INSTITUTE

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SPECIAL  
ISSUE

## BISMUTH: THE AMAZINGLY "GREEN" ENVIRONMENTALLY-MINDED ELEMENT

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Bismuth is a relatively rare metal found in the earth's crust at about the same abundance as silver and almost never occurring in the native state. It is usually associated with copper, lead, tin, wolfram, silver, and gold ores.

It is mostly found in Australia, Bolivia, Canada, China, Japan, Korea, Peru, Mexico, the United States and Yugoslavia. The USSR does not appear to have more than a nominal quantity and must heavily rely on imports. Bolivia and China are the only lands where native Bismuth is available, but its exploitation costs can be high. World production currently stands at about 4,000 tons per year.

Bismuth metal is soft, heavy, brittle, and silvery white with a pinkish tinge. It melts at 271°C (520F), has a density of 10.067 grams per cubic centimeter on melting point, expands by 3.32% on solidification, and boils at 1560°C (2840F). Its atomic number is 83 and the atomic weight 209. It has the lowest thermal conductivity of all metals, except mercury, while its electrical conductivity is greater in the solid than in the liquid state.

In a world in which practically everything — including the air we breathe and the water surrounding us — presents some sort of hazard bismuth metal is one of those rare elements considered safe *for it is non-toxic and non-carcinogenic notwithstanding its heavy metal status.*

### BACKGROUND

Although it was not yet known as a metal, Bismuth was probably used as a beauty care product during the antiquity, also, traces can be found in Greek and Roman coins.

It was first mentioned in 1450 as *Wismutton* or *Bisemutum*, probably from the old German word *Weissmuth*, meaning *white substance*.

Shortly after, circa 1476-1534, the relatively high Bi content - 18% - found in a bronze knife from Machu Picchu suggests that the Incas included it for specific metallurgical purposes.

Around that time, Europeans started using it in paints, or in alloys for dishes, trays, and containers for the preservation of wine. Since it enhanced castability and wear resistance of type-print, Bismuth brought a definite improvement to the emerging art of printing.

However, it was still obscure to alchemists of the XVII<sup>th</sup> Century who confused it with zinc, tin, or antimony and little did they know — as scientists realized only recently — that it could be converted into gold!

Even during the XVIII<sup>th</sup> Century the knowledge of Bismuth was very limited, and it was only during the last quarter that

the physical properties, its chemical reactions, and its salts were closely investigated. That brought a diversification of uses casting a sharper focus on its properties.

As the process continued and kept expanding, it has brought a profusion of information likely to create a new kind of obscurity through an excess of technicality because of the element's ability to thrive on evolving technology.

## MAJOR APPLICATIONS

### Pharmaceuticals

For nearly 150 years, low doses of Bi compounds have been considered excellent remedies against gastric disorders, i.e. colitis, diarrhea, peptic ulcers. They were, and still are, used for burn bandage dressings, antiseptic powders, salves or ointments and the treatment of venereal diseases.

However, Bismuth medication keeps making amazing strides nowadays too and its newly discovered properties surpass those of so-called "modern" molecules. It is the only known active ingredient eradicating *Helicobacter* (formerly identified as *Campylobacter*) *Pyloridis*, a bacteria inflicting ulcers and this is paving the way to a number of specialities doctors world-wide will be able to prescribe soon, either on their own or in association with antibiotics.

Meanwhile, current investigation demonstrates that Bismuth-compound pre-treatment reduces the lethal toxicity of several forms of cancer therapy and can possibly help combat AIDS.

Moreover, Bismuth compounds are increasingly added to special polymers for bone implants, dental prosthetic devices, catheters... to make them detectable to X-rays in full safety. An unexpected bonus in these times prone to terrorism is that plastic firearms can be made detectable too!

For years already, diagnostic devices (scanners) have been using Bismuth Germanium Oxide (BGO) crystals to neutralize lethal gamma rays and improve overall imaging, and a recent development shows that a similar promise will be fulfilled with the burgeoning of Bismuth-based superconductors (cylinder for electro encephalography).

### Metallurgical Uses

**Steels.** Bismuth addition improves the machinability of free cutting steels. Evenly dispersed in the alloy, the tiny Bi droplets melt upon contact with the cutting tool, lubricating it. Also, they cause the chips to break off, which prevents built up edge, helps get rid of excess heat, and increases turning speed.

Clearly, this application is expanding as world demand for specialty steel products strengthens, and as stronger environmental pollution regulations curbing the use of lead come into force. Thus, once more, the determining bearing of *non-toxicity*.

**Aluminum.** Bismuth improves the machinability of free-cutting aluminum in a fashion similar to steels : It also improves corrosion and stress resistance and reduce the need to use chlorine to eliminate sodium during processing of specific alloy grades.

**Copper.** Nowadays, safety considerations about lead in our drinking water system encourage the use of Bismuth in free-cutting copper for plumbing fittings.

**Iron Castings.** Inoculations of minute amounts of Bi improve the characteristics of castings used by the automotive, and machine tools and parts industries. It helps increase the wear-resistance, doubles the life of parts, and reduces costly annealing cycles of malleable irons among others.

More recently, the ability to exert more precise control over the amount of potentially deleterious additives has created demand for **spheroidal graphite (SG) castings** with greater shock resistance and tensile properties.

**Fusible Alloys.** Bismuth combines with one or several elements such as antimony, cadmium, indium, gallium, lead, tin... To form alloys melting as low as at 20°C (68°F).

Because it expands on solidification, it can be dosed to produce dimensionally stable alloys. As a rule of thumb, alloys with more than 55% Bi expand, those with less than 48% contract. Mixtures in the remaining gap being dimensionally stable.

These fundamental principles are exploited to produce a wide range of fusible, or low-melting point alloys as often referred to, which composition can be manipulated to meet the most stringent requirements.

They suit such varied purposes as dip-casting, tube bending, lens blocking, positioning of jet engine blades, punches and dies, lost wax castings, sprayed precision mouldings... to name but a few. Low-melting alloys are also found in heat-treatment baths for tempering tools, chain links, or special steel strip for springs and razor blades.

They can be re-used, with little or no loss and their applications are only limited by man's ability to find solutions to the most complex applications.

Moreover, there are many other end-uses, i.e. solders, conventional, or with melting points low enough to eliminate heat damage to sensitive micro electronics, fabrics,

plastics, and foods. They also make permanent seals for multi-glazed insulating panes. Not to forget safety devices melting at predetermined temperatures : fuses, water sprinklers, safety valves...

Furthermore, the next generation of electrical contact material is based on Silver-Bismuth compositions suitable for the building and the automotive sectors because they resist wear, do not weld or produce arcing under heavy loads.

### Electrochemistry

Small Bi additions to tin electroplatings prevent tin-pest, a phenomenon causing tin to decompose into grayish powder at low temperatures. This is applied as a bearing alloy coating internal combustion engines of cars and tractors, or couplings and special gear destined for cold climates.

There are also regular or rechargeable battery cells offering an environmentally-gentle alternative to nickel-cadmium, with higher density and longer life too.

### Electronics

Ceramics represent a vast outlet for Bi-compounds, particularly Bi-trioxide. Generally, small levels of inclusions have a remarkable impact on the performances of the materials, i.e. zinc oxide varistors 100-fold superior than the devices they replace, yet totally ineffective without Bi! Originally applied to high voltage ceramics, this use is now expanding to low voltage and DC current devices.

More substantial inclusions lower the processing temperature of ceramics from a typical 1400°C (2500°F) to around 1000°C (1800°F) and below. Aside from easier handling and energy savings, the lower temperatures allow the use of cheaper components.

Many of these ceramics keep a silent vigil over our safety by detecting fluids or gases while partial pressure oxygen sensors monitoring reduce the energy uptake.

Optical glasses are similarly improved, and major amounts of mostly Bi-oxide impart higher specific gravity or greater refractive indices. Glassy compounds or simply calcined Bi oxide are also baked on ceramic bodies, for insulating or specific conduction purposes.

Typical of the world of electronics, this range of applications is in a constantly growing expansion pointing to exciting new horizons in the realm of optoelectronics, or the revolutionary "warm" superconductors which, as outlined above, improves our well-being too.

### Plastics

Bismuth compounds impart flame-retardant or smoke-inhibiting properties to plastics. Their substantial advantages are a fundamental action at the molecular level which does not degrade in time or use, a deodorizing effect of the bad smelling additives, less corrosion of the processing equipment. Not to forget greater color and aging stability.

Used mainly in Europe the limiting factor remains, so far, the lack of stronger safety regulations governing the use of plastic materials in public places. However, they are bound to come into force sooner or later, mostly spurred by tragic accidents, unfortunately!

Bi-compounds are also used as stabilizers, plasticizers and additives of some sort, while investigation goes on.

Another development concentrates on the unique conduction properties of the metal to produce plastics with built-in shielding protection against electromagnetic or radio-frequency interferences (EMI-RFI) and electrostatic discharges (ESD) creating serious disturbance to the electronic equipment surroundings us.

Not to forget the medical applications already reviewed.

### Chemicals

Bismuth catalysts are widely used in industrial organic chemistry. The major outlet is for the production of acrylonitrile and acrolein, involving mostly a Bi-Mo catalyst.

Lately, a new breed of catalysts alleviates the use of CFCs for polyurethane foams.

Bi-compounds go also into paint dryers, synthetic rubber vulcanizing accelerators, reagents, stabilizers, tracers... And a developing whole new range of products which is as much part of electronics deals with a broad choice of surface coatings for magnetic, acoustic, optical, or a combination of the three recording modes. This propels Bismuth in the world of computers as well as photography, or rather "reprography".

Elsewhere, the adoption of Bismuth eliminates marine-life pollution arising from the use of organotin compounds

### Pigments

There is a wide variety of pigments ranging from cosmetics to the coloration of glass, decorative glazing, enameling and metallic paints, as well as UV or heat-absorbing coatings for outer space and strategic applications.

Bismuth oxychloride (BiOCl) pigments are best known, worldwide, for their truly exceptional pearlescent, nacreous effect in cosmetics, i.e. lipsticks, nail varnishes, make-up powders.

Their brilliance and luster surpasses that of guanin, the natural product they replace, and which is much more expensive because the fish-scales from which it is extracted are scarce, thus expensive.

The recent development of UV-stable Bi-oxychloride suitable for plastics gives a very distinctive look and beneficially replaces toxic pigments.

The incorporation of Bismuth to hair dyes not only adds color but deodorizes them.

For, again, Bi compounds are non toxic and this has been spurring demand for non-pearlescent Bismuth-Vanadate yellows, greens, and reds, from Europe, the US, and China as the shrinking world community seeks a safe alternative to cadmium.

In fact, their variations are also used for ceramic cooktops, oven or toaster-oven heated glasses in which they induce reversible color changes indicating when the temperature of the surfaces is safe to the touch.

### Ecological Considerations

As ecological considerations make it imperative to shift to safer practices, a primary target is to remove lead wherever it can prove unsafe. Because Bismuth possesses most of its properties but is perfectly safe to use, this has been creating a growing demand in such diametrically different applications as substituting Bi for Pb for determining the purity of gold in fire assays used since time immemorial, including it in glasses, ceramics, glazes, lubricating oils and greases, , potable water distribution fixtures, aerosols or PU foaming catalysts

doing without CFCs, quite sophisticated — yet simple — energy-conserving devices...

Moreover, as it became clear that the lead shot unwittingly discharged over water bodies by hunters eventually seeps deep into the ground to pollute water supply, even the sportsman is discovering Bi as the ideal substitute when it comes to shooting waterfowl.

### CONCLUSION AND OUTLOOK

This enumeration could go on at great length but we have seen by now that hardly any walk of life remains untouched, directly or indirectly, by Bismuth. Be it pearlescent soaps, reagents for the purification of sugar, tracers for surgical sutures or window glass panes, thermochromic safety coating indicators, energy-saving lightbulbs, binders for grinding wheels, permanent magnets, ferrites, silverless photographic or X-ray films, thermoelements, energy-converting films, nuclear reactor cooling fluids and seals, explosives for oil and gas exploration, safety flares for distress signals. Even Roman coins, the Statue of liberty, or Mecca's holy Zam Zam spring water contain bismuth!

The striking factor linking this ever-expanding range of applications is the exceptional physical absorption properties of Bismuth and its compounds which makes it thrive in this demanding world of evolving technology.

In whatever form it is used, whether it goes in metallurgical additives, pharmaceuticals, chemicals or alloys, a little amount of Bismuth retains the ability to introduce fundamental changes in the mechanism of action.

*In the final analysis however, the element's most exceptional property may well reside in the fact that, whatever its application, it invariably exerts a beneficial influence on human health as it leads to safer, energy-saving, environmental conservation practices.*

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