

1. Antimony

Antimony is a semimetal, which can usually be found in its most stable metallic form. In its metallic form it is physically bright, silvery, with a metallic lustre and average hardness and brittleness. Antimony is a poor conductor of heat and electricity. Antimony and many of its compounds are toxic.¹

Antimony is mined both as a main metal and as a by-product: The main antimony ore is antimony sulfide (stibnite), but lead and copper ores often contain antimony, which is concentrated as a by-product and obtained during the recovery of the main metal. Antimony is recovered in its metallic form from ore primarily through pyrometallurgical techniques.^{2,3} The production of antimony is currently concentrated mainly in China and the average price of antimony metal was about 3US\$/kg in 2011* (see also Figure 2).⁴ After a peak in 2011, the price has been generally decreasing over recent years.⁵

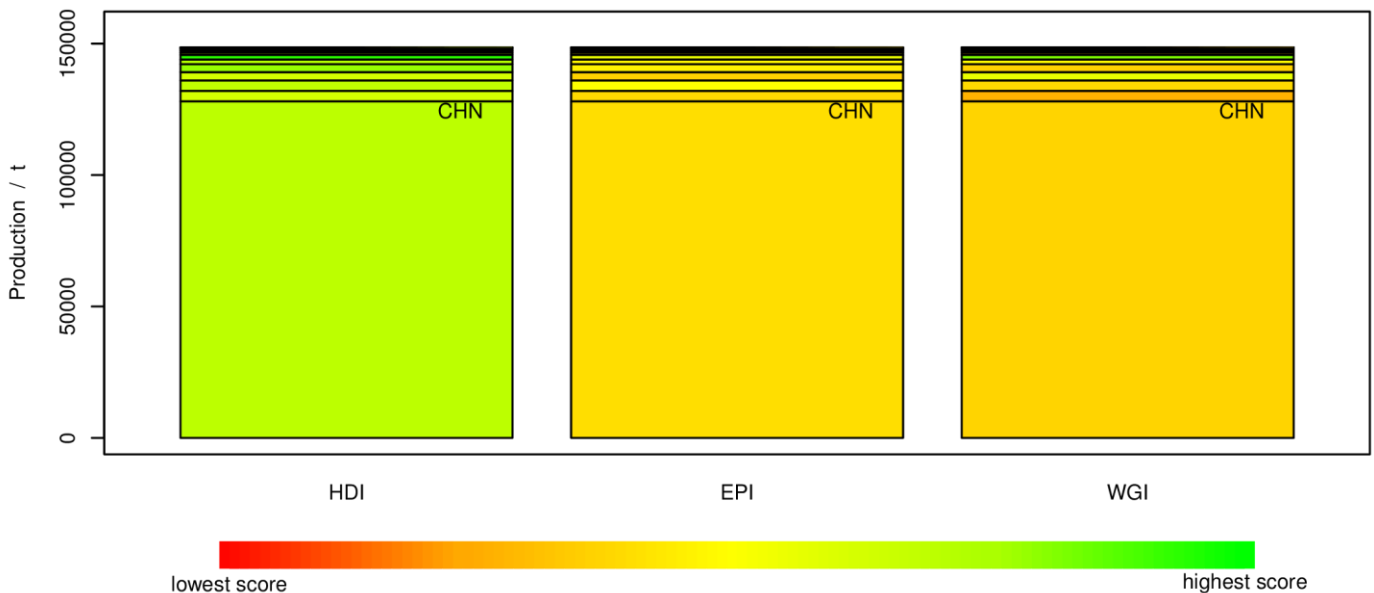


Figure 1: Distribution of antimony production⁶ and corresponding scores of the producing countries in the Human Development Index (HDI),⁷ Environmental Performance Index (EPI),⁸ and World Governance Indicators (WGI).⁹ Both the EPI and WGI are used to assess supply risks with the EU methodology for determining critical raw materials.¹⁰ CHN = China.

* New York dealer price for 99.5% to 99.6% metal, c.i.f. U.S. ports.

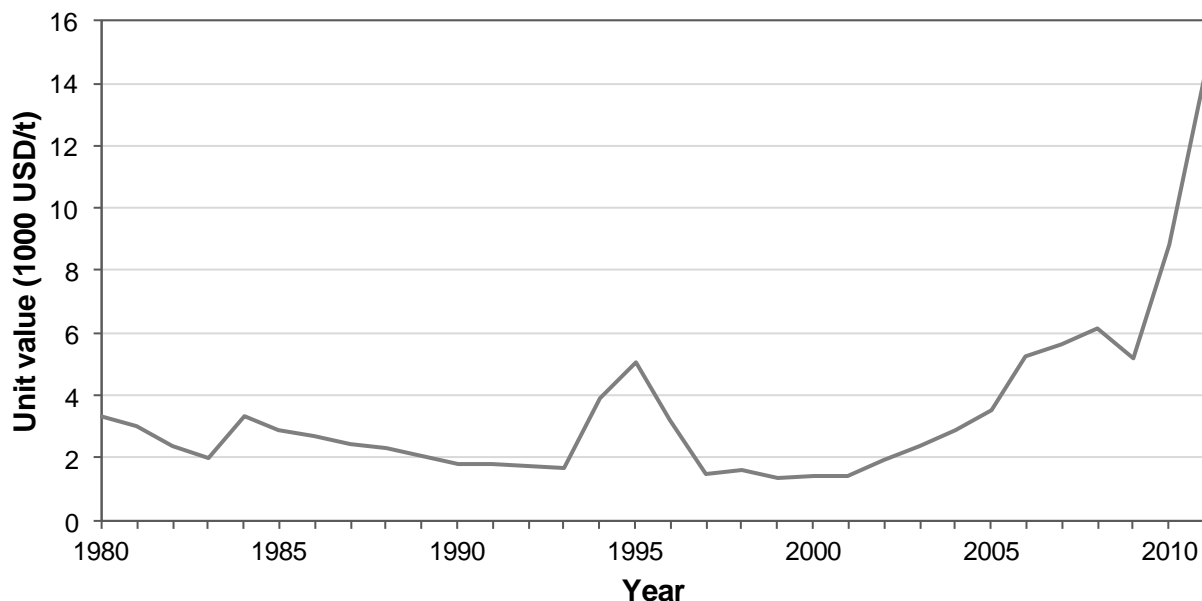


Figure 2: Antimony price development during 1980 – 2011. The unit value of antimony reports the value of 1 metric ton (t) of antimony apparent consumption (estimated).¹¹

Uses and Substitutability

Flame retardants

With a share of 71% of antimony consumption, antimony as antimony trioxide is mainly used for flame retardants. The main applications within this sector include polyvinylchloride (PVC) for conveyor belts for example in mines, cable coatings; coated fabrics for wall coverings and cushion covers, among others. Moreover, it is used as high impact polystyrenes for television backs and domestic electrical appliances, as well as housings for electrical equipment (including PCs). Polyethylene and propylene is primarily used for wire sheathing and electrical conduits in buildings. Polyamides and engineering plastics such as nylons for automotive uses, industrial equipment, and electric moulded parts as well as unsaturated polyesters for applications such as building panels, automotive parts, and lifeboat hulls are further typical uses of antimony.²

When antimony trioxide is combined with a halogen, flame retardant properties are imparted to several materials through the formation of halides. Antimony halides promote reactions that cause the formation of carbonaceous char rather than volatile gases. This char then acts as a heat shield that retards the breakdown of the plastics, thus preventing the release of flammable gases.²

Antimony trioxide can be substituted with selected organic compounds, hydrated aluminum oxide or mixtures of zinc oxide and boric oxide.^{4,12} However, while substitutes are available, in general, antimony is seen to offer superior performance.

Lead alloys²

The second largest application for antimony is in lead alloys, making up a market share of 9%. Due to its weak mechanical properties, it is mainly used in numerous alloys with lead and tin. The final use of the

alloy is determined by both the percentage of antimony in the alloy as well as the other compounds present.

For antimonial, or hard, lead alloys containing antimony between 1-15%, the presence of antimony results in an increase of tensile strength, rendering the material more robust to stresses enforced by charging and discharging reactions. Antimonial lead alloys that contain 1-9% of antimony are used for cable sheathing and lead pipes, whereas the same alloys with 7-12% antimony are used for storage batteries and with an antimony content of 12-15% they are used for small-arms ammunition.

Antimonial lead alloys with an antimony content between 1.5-3% are mainly applied for grid plates, straps, and terminals of lead-acid batteries. Here, the addition of antimony improves fluidity, making the casting of battery grids easier. Tensile strength is also increased, as is the electrochemical stability of lead.

Babitt metals include both ternary tin-antimony-copper alloys and quaternary tin-antimony-copper-lead alloys, in both cases with a share of antimony ranging between 4.5-14%. Babitt metals are applied in low load bearings. The addition of antimony to the alloy results in good anti-seizure properties and corrosion resistance on the one side but low fatigue strength on the other side. Heavy load bearings, which require a higher fatigue resistance for applications such as railways, use quaternary tin-antimony-copper-lead alloys with an antimony share between 8 and 15%.

Type metals are antimony-lead alloys containing 2.5 – 25 % antimony. These alloys are used in the printing industry and the antimony is added in order to lower the casting temperature, increase the hardness and minimize shrinkage during freezing.

Brittania Metal and Pewter contain 7 - 20% antimony which increases the hardness of the metal and allows a highly polished surface to be obtained. These metals are used for the manufacture of vases, lamps, candlesticks, tea and coffee services, and other decorative applications.

Tin-lead alloys with an antimony share of less than 1% are used for soldering, whereby the antimony increases the hardness of the alloy.

Antimonide contains, in addition to antimony, indium, aluminum and gallium. Antimony is added due to its electrochemical properties as the applications include dopants in semiconductors for infrared detectors, Hall-effect devices and diodes.

In general, combinations of cadmium, calcium, copper, selenium, strontium, sulfur and tin can substitute antimony in most lead alloys.⁴

Rubber

For the vulcanization of red rubber compounds, a 7% share of antimony is utilized. Antimony pentasulfide, Sb_2S_5 , adds the required flexibility.² It is difficult to substitute.¹³

Glass

The glass industry represents a 5% share of antimony use in the form of sodium hexahydroxyantimonate. This compound is prepared by melting antimony or antimony oxides with excess sodium nitrate and is used as an opacifier for glass and enamels.² Glass containing antimony trioxide or sodium antimonate is used for television tubes, as the oxide removes color and gas bubbles. Substitutes include compounds of chromium, tin, titanium, zinc and zirconium.⁴ Therefore, it is comparatively easy to substitute.¹³

Catalysts

Catalysts make up 4% of antimony use, mostly for the polymerization catalyst in the manufacture of polyester fibres, which requires antimony trioxide.² A potential substitute is titanium catalysts, which can be inactivated when a dulling agent is applied. There are some concerns around heavy metals in plastics leaching e.g. into drinking water. However, titanium catalysts are not expected to replace antimony in PET production to a significant extent with 2020 as a time horizon (even though alternatives exist at the R&D stage) as there is no regulatory pressure from the FDA or the EC. Therefore antimony is assumed to be currently difficult to replace.¹⁴

Pigments & Others²

Pigments and other applications for antimony result in a 4% antimony use. Chromate pigments apply antimony trioxide for its unique pigmentation properties. However, compounds of chromium, tin, titanium, zinc and zirconium could be used as substitutes.⁴ Another use for antimony is as an opacifier for ceramic glazes and as a frit. Antimony trioxide is used in these applications as well. Antimony is comparatively easy to substitute in its use for pigments.¹³

Summary

The demand for antimony is dominated by its use in flame retardants (as antimony trioxide). Because the applications—and requirements—vary widely, there are options for substituting antimony trioxide partially or, in some cases, completely. Also, substitutes are available for its use in lead alloys, glass & pigments, apparently with limited loss of performance or additional costs. This is not the case for rubber and catalysts, where the use of antimony brings substantial advantages in either performance or costs.

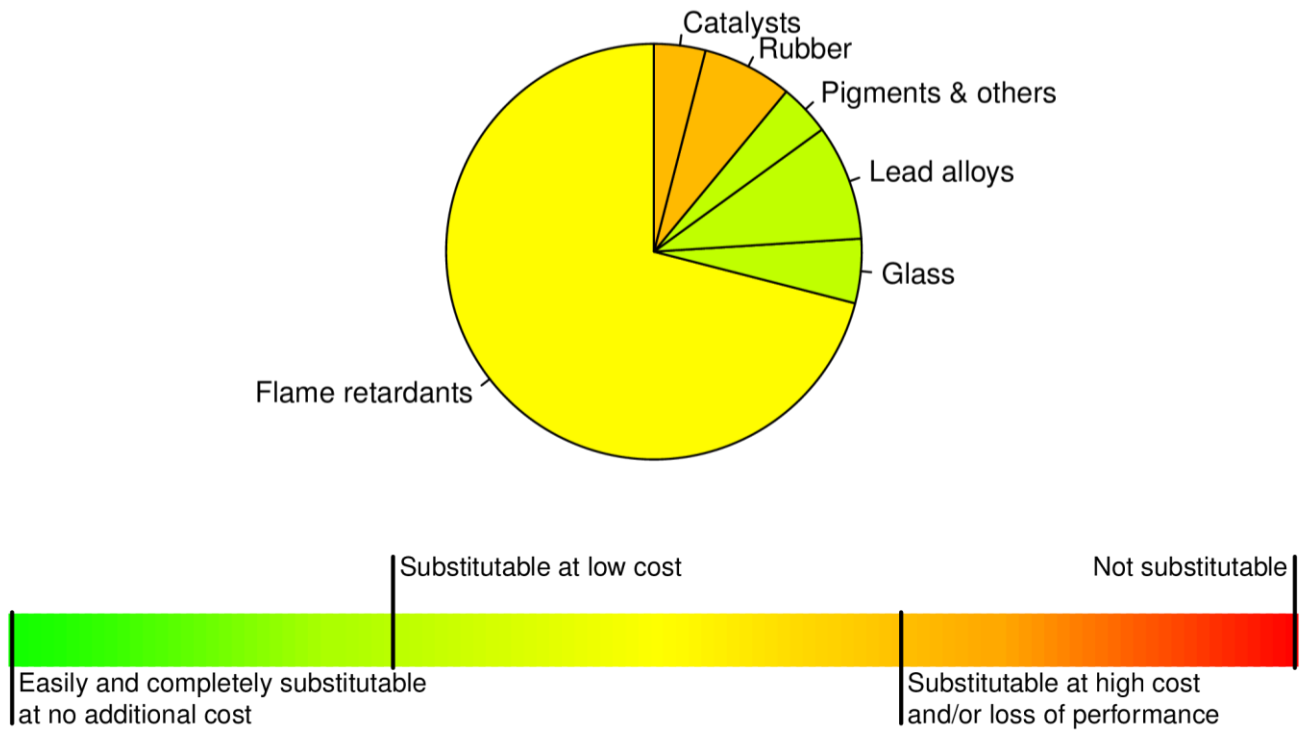


Figure 3: Distribution of end-uses and corresponding substitutability assessment for antimony. The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010).

References

- 1 Haynes WM (ed.) (2012) CRC Handbook of Chemistry and Physics, 93rd edn.: Taylor & Francis
- 2 Grund, S. C., Hanusch, K., Breunig, H. J., Wolf, H. U. (2006) Antimony and Antimony Compounds, in: Ullmann's Encyclopedia of Industrial Chemistry, pp. 11–42. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA
- 3 Buttermann W.C., Carlin JF, JR. (2004) Antimony. Open-File Report 03-019
- 4 Carlin, J. F., JR. (2013) Antimony, in: U.S. Geological Survey (ed.) Mineral commodity summaries 2013, pp. 19–20
- 5 Metal Bulletin Antimony MB free market in warehouse \$ per tonne monthly average: Latest Metal Prices Tracking and Comparison Tool. <http://www.metalbulletin.com/My-price-book.html?price=34138>. Accessed 3 September 2013
- 6 Reichl C, Schatz M, Zsak G (2013) World Mining Data: Production of Mineral Raw Materials of individual Countries, by Minerals. in 2011 in metric tonnes
- 7 United Nations Development Programme (UNDP) (2013) The 2013 Human Development Report – "The Rise of the South: Human Progress in a Diverse World"
- 8 Yale Center for Environmental Law and Policy (YCELP) (2013) Downloads | Environmental Performance Index. <http://epi.yale.edu/downloads>. Accessed 26 July 2013
- 9 World Bank Group (2013) Worldwide Governance Indicators. http://info.worldbank.org/governance/wgi/sc_country.asp. Accessed 26 July 2013
- 10 Ad-hoc Working Group on defining critical raw materials (2010) Critical raw materials for the EU: European Commission
- 11 Buckingham, D., Carlin, J., JR. (2012) Antimony: Supply-Demand Statistics, in: U.S. Geological Survey Minerals Information
- 12 Borax Firebrake ZB: An unique zinc borate combining the optimum effects of zinc and boron oxides and water release for developing fire retardant formulations processable up to 290 °C. <http://www.borax.com/product/firebrake-zb.aspx>. Accessed 28 August 2013
- 13 Eurometaux (2013) Antimony Substitutability. personal notification
- 14 Joce C (2013) Antimony Substitutability. personal notification