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# A REVIEW
# OF THE
# PRODUCTION AND USES OF ARSENIC.

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## 1. INTRODUCTION.

Although a number of arsenic minerals such as arsenopyrite ($Fe\ As\ S$); orpiment ($As_3\ S_3$), and realgar ($As_2\ S_2$) are known, commercial supplies of arsenic are obtained almost entirely as a by-product from the gases evolved during the roasting of metallic ores containing arsenides and sulpharsenides, particularly those of lead, copper, gold and tin. The name 'arsenic' should be reserved for the metallic element, but in commerce it is frequently used to designate arsenious oxide $As_2O_3$ or white arsenic, a practice which is followed in this review.

## 2. WORLD PRODUCTION.

The countries which marketed the largest quantities of white arsenic ($As_2O_3$) in 1950 were:

| | | |
|---|---|---|
| United States .................... | 11,851 | tons |
| Mexico ........................... | 8,845 | " |
| Sweden ........................... | 2,870 | " |
| France ........................... | 2,800 | " |
| Belgium* ......................... | 1,879 | " |
| Western Germany* ................. | 1,106 | " |
| Brazil ........................... | 1,050 | " |
| Italy ............................ | 670 | " |
| Portugal ......................... | 598 | " |
| Spain ............................ | 472 | " |
| Australia ........................ | 200 | " |

*Figures for Germany and Belgium are for exports only.

Arsenic is also produced in the U.S.S.R., China and Korea.

During World War II, some countries, such as the United States and Mexico, more than doubled their output of arsenic, and a newcomer, Peru, achieved an output of 6,800 long tons in 1944. Statistics of arsenic production are not complete, but the world output probably amounts to about 42,000 long tons per annum. The output of arsenic attainable from the Boliden gold mine in northern Sweden greatly exceeds market requirements, as the ore carries about 10 per cent. of $As_2O_3$. Much of the arsenic extracted is either stored or mixed with concrete and dumped into the sea.

Most of the white arsenic recovered in the United States is obtained during the smelting of copper and lead ores, such as those at Butte (Montana) and Tintic (Utah). In Australia the chief occurrences of arsenic were the now-defunct Wiluna and Moonlight gold mines in Western Australia.

The production of arsenic in Canada increased considerably during World War II, being derived principally from the treatment of gold and lead ores.

Only small quantities of white arsenic and arsenical soot are recovered in Great Britain, usually less than 100 tons per annum, and hence the demands of industry have to be met by imports which, in recent years, varied between 3,000 and 7,500 tons per annum, the total for 1951 being 6,780 tons.

The country consuming the greatest quantity of arsenic is the United States, which normally augments her domestic production by imports. In 1950 her apparent consumption of white arsenic was 28,660 tons.

## 3. AUSTRALIAN PRODUCTION.

The Australian production of arsenic trioxide, formerly a by-product of gold mining operations, ceased in 1952. Since then, all domestic requirements have been met by imports.

IMPORTS INTO AUSTRALIA OF ARSENIC TRIOXIDE AND PENTOXIDE (Tons).

| Country of origin | Trioxide | | | | Pentoxide | | | |
|---|---|---|---|---|---|---|---|---|
| | 1954 | 1955 | 1956 | 1957 | 1954 | 1955 | 1956 | 1957 |
| U.K. .......... | 5 | - | 20 | 1 | 3 | 16 | - | - |
| France ....... | 600 | 932 | 754 | 434 | - | - | - | - |
| Portugal ..... | 576 | 907 | 440 | 265 | - | - | - | - |
| Sweden ....... | 1,143 | 1,517 | 895 | 854 | - | - | - | - |
| Others ....... | 324 | 136 | 61 | 32 | - | - | - | - |
| Total: | 2,648 | 3,492 | 2,170 | 1,586 | 3 | 16 | - | - |
| Value (f.o.b.) | £130,683 | 175,909 | 100,405 | 66,614 | 263 | 1,470 | | |

The domestic price of arsenic is governed by the landed cost. In the United Kingdom the price of the metal throughout 1957 and up to August, 1958, was £Stg.400 per ton, and of white arsenic (98-100 per cent $As_2O_3$) £Stg.40-45 per ton.

The United States price for white arsenic has remained unchanged since 1952 at 5½ cents per pound.

## 4. USES OF ARSENIC.

It is estimated that the world usage of arsenic is distributed as follows:-

| | |
|---|---|
| 73 per cent. | in insecticides |
| 20 per cent. | in weed killers |
| 3 per cent. | in glass manufacture. |
| 4 per cent. | miscellaneous, including drugs and metallurgical uses. |

An indication of the relative quantities of arsenical compounds consumed by various trades is afforded by the statistics issued by the United States Bureau of Mines. In 1950 the amount sold as insecticides comprised 17,634 tons of lead arsenate and 21,205 tons of calcium arsenate, but the quantity used in "Paris Green" was not stated. Wood preservatives in the form of "Wolman Salts" containing 25 per cent. of sodium arsenate accounted for 534 tons, whilst the amount of zinc meta-arsenate used for the same purpose is not stated, but possibly amounted to about 600 tons. The figures for arsenic used in drugs are not published, but may have totalled about 470 tons. The apparent consumption of white arsenic in the United States in 1950 amounted to 28,664 long tons.

Calcium arsenate can be made by the process developed by the U.S. Department of Agriculture, in which arsenic trioxide is oxidised to the pentoxide by means of nitric acid, the solution neutralized by caustic soda to form sodium arsenate, and from this calcium arsenate is prepared by adding milk of lime.

Lead arsenate can be made by fusing white arsenic with either caustic soda or a mixture of soda ash and sodium nitrate, dissolving the melt in water, and adding a solution of lead nitrate or acetate to precipitate lead arsenate.

### 4.1 Insecticides and Weed Killers:

Arsenic compounds are widely employed as insecticides and fungicides, often in the form of calcium arsenate, calcium arsenite, lead arsenate or Paris Green (copper acetate and arsenic). The form often favoured for combating the boll weevil in cotton cultivation is calcium arsenate, the consumption being about 5 lb. per acre of plants. Arsenical weed killers usually consists of sodium arsenite, which is also the form in which arsenic is used in sheep and cattle dips. These uses account for about 70 per cent. of the world production.

Insecticide makers usually require a free-running product of fine particle size containing 98 per cent. or more of $As_2O_3$ with only traces of antimony. Makers of weed killers require a white product of not too fine particle size.

### 4.2 Wood Preservation:

Arsenic, in various forms, is used for the preservation of telephone poles, mine timbers and railway sleepers.

### 4.3 Glass Making:

It has been estimated that about 25 per cent. of the white arsenic consumed in the United States is used in the manufacture of opal and opalescent glass. White arsenic is sometimes used as an oxidizing agent in glass making to overcome the greenish colour caused by iron compounds.

The glass industry usually requires a white arsenic containing 96 to 99.5 per cent $As_2O_3$ and has a preference for a dense product of fairly coarse particle size. Iron content must be low.

### 4.4 Metallurgical Uses:

The metal can be produced by heating a mixture of white arsenic and charcoal in a closed gas-fired furnace and condensing the volatilized metal.

Probably the most important use for metallic arsenic is as an addition to copper to increase its resistance to corrosion and erosion. Arsenical copper is much used in Europe for locomotive fire box stays and plates, but in the United States, steel is often preferred for the purpose. Arsenical copper is also used in motor car radiators and similar copper parts which have to be assembled by soldering, as arsenic raises the annealing temperature so that the plates do not lose strength.

Metallic arsenic is sometimes added to lead shot to the extent of 0.4 per cent. to assist in the formation of truly spherical pellets. The metal has also been added to solder, and is a useful component of lead-base alloys used for electrical storage battery grids.

### 4.5 Other Uses:

Arsenic is used to a small extent in medicine as potassium arsenite and Erlich's 606 and in preservatives for treating animal hides.

## 5. TREATMENT METHODS.

### 5.1 Refining Arsenical Dust:

All the white arsenic of commerce is obtained by treating the arsenical soot which condenses in flue dust collecting systems and chimneys during the roasting of ores containing arsenic. As arsenious oxide or white arsenic begins to condense at a temperature of about 218° C., it collects mainly in the cooler parts of the flue system. Lead baghouse products containing 30 per cent. of white arsenic and copper furnace and roaster dusts carrying from 20 to 30 per cent. are not uncommon.

Various processes are in use for the refining of crude arsenical dust, one being to roast the dust on the hearth of a Brunton furnace after adding a small quantity of sulphide ore, e.g., pyrites, to prevent the formation of nonvolatile arsenites in the residue from the roast.

The gases from the furnace are passed through a series of chambers in which white arsenic of 90 to 95 per cent. purity condenses. This crude white arsenic is further purified by being resublimed in reverberatory furnaces operating at about 550° C. to obtain a product of over 99 per cent. purity.

### 5.2 Mineral Beneficiation:

The most important minerals of arsenic from the economic standpoints are the sulphides, particularly arsenopyrite, which can be concentrated by flotation. At Wiluna (W.A.) gold is associated with both iron and arsenic minerals, the recovery of the latter being effected by flotation in alkaline circuit with large quantities of copper sulphate and xanthate. Arsenopyrite appears to require more oxygen than is normally needed in the preparation of pulps for flotation. Heavy-metal pulp to which a sulphide ion has been added must be freed of this excess sulphide before good flotation of the arsenopyrite can be effected. Dichromates, permanganates and bromine water have been used experimentally with some benefit in sulphide pulps to remove this excess sulphide, but such use is rare in operation. They must be used sparingly and should be exhausted before reducing-type collectors are added to the pulp.

Depression of arsenopyrite is in some cases obtained by the use of either sodium or potassium cyanide in the presence of sulphydric collectors.

The concentration of arsenical minerals by table flotation has also been investigated by several researchers. The selective oiling of mineral surfaces and the subsequent launching of oiled particles at an air-water interface has been known from the earliest of times. The significant point regarding this "skin" flotation is the relatively large size of particle that can be floated off in this manner. Oiled particles tend to "skin" float, and furthermore, in passing over and along the riffled deck of a shaking table, submerged oiled particles break through the surface of the water and are carried off with the cross-water. This "skin" float effect can be increased by the use of air or water jets impinging onto the table deck.

## 6. CONCLUSIONS.

It is evident from a survey of available literature that the main source of arsenic throughout the world is as a by-product from the smelting industry, where the treatment of ores containing arsenic is undertaken. It would also appear that, because of the current price and demand for the product, any attempt to beneficiate an ore for its arsenic content alone would be uneconomic.

With reference to the Taliska mine in South Australia, the ore is reported to have the following composition:

| | |
|---|---|
| Lead .......... | 7.0 per cent. |
| Arsenic ....... | 19.1 " |
| Silver ........ | 3 oz. 16 dwts. |
| Gold .......... | Trace |
| Zinc .......... | " |

It is considered that any work done on material from this mine should be undertaken with a view to the production of a lead concentrate containing as much silver and arsenic as possible. The arsenic content of such a concentrate would then be recovered during smelting operations.

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