Mineral Resources
Consultative Committee

Mineral Dossier No 2

Barium Minerals

Compiled by
R S Collins PhD, DIC, BSc, FGS, FRGS
Mineral Resources Division
Institute of Geological Sciences

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Titles in the series

No 1 Fluorspar
No 2 Barium minerals

Preface

The Mineral Resources Consultative Committee consists of representatives of interested Government Departments, and specialist advisers. It was set up in 1967 to keep present and future requirements for minerals under review and to identify problems associated with the availability, exploitation and use of mineral resources, both inland and offshore, having regard to competing demands on land use and other relevant factors.

Widespread and increasing interest in the mineral resources of the United Kingdom has led the Committee to undertake the collation of the factual information at present available about those minerals (other than fossil fuels) which are now being worked or which might be worked in this country. The Committee has produced a series of dossiers, each of which was circulated in draft to the relevant sectors of the minerals industry. They bring together in a convenient form, in respect of each of the minerals, data which had previously been scattered and not always readily available. These dossiers are now being published for general information.

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Introduction

This dossier on barium minerals covers a wide range of topics ranging from the mineral in the ground to the manufactured product prepared from the mineral. It is arranged in three parts: Part I is a detailed study of barytes, the main raw material of the barium chemical industry; Part II covers minor natural sources of other barium raw materials, of which witherite is of considerable interest because until 1969 the UK was for many years the principal world producer; Part III provides a summary of the production and utilization of barium chemicals, and of other derived materials which are of recent development and play an important role in the electronics industry.

Metric units are employed throughout this document except where otherwise stated. In most cases this has necessitated the conversion of originally non-metric data. The units and conversion factors are as follows:

millimetres (mm) = inches x 25.4
metres (m) = feet x 0.3048
kilometres (km) = miles x 1.609344
square kilometres (sq km) = acres x 0.404686
grammes (g) = troy ounces x 31.1035
kilogrammes (kg) = pounds x 0.45359237
tonnes (1000 kg) = long tons x 1.01605

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Summary

Barytes, barium sulphate, a heavy, inert industrial mineral, the main raw material for the production of barium chemicals and derivatives, occurs in veins in the older rocks in many parts of the British Isles, commonly associated with non-ferrous metal ores. Although it was formerly mined in several areas, there is now only one locality, Closehouse in the North Riding of Yorkshire, where barytes is now mined for chemical uses. An increasing quantity of barytes is becoming available in Derbyshire as a flotation by-product of fluorspar production, but this material has so far been unsuitable for most chemical uses.

The main world use of barytes is in heavy muds for gas and oil well drilling. There is an increased United Kingdom requirement for this material, which is in part being satisfied by increased flotation production in Derbyshire. The United Kingdom is dependent on imports for about three-quarters of the barytes requirements, and also imports barium chemicals. The barium industry is liable to fairly rapid and violent swings in requirements and the extractive industry has for some years been under-capitalised because a better return on capital could be obtained elsewhere.

Witherite, barium carbonate, is a minor industrial mineral which until recently was produced almost exclusively at only one mine in the world, Settlingstones in Northumberland. This mine closed in 1969 and the mineral is no longer produced anywhere, so far as is known. Witherite was once a favoured raw material for some chemical production, and was also used in the brick industry.

Barium chemicals are used in the glass, ceramic, and electrical industries. The most important of these chemicals is the carbonate, also known as synthetic witherite. The requirements for this substance have increased in recent years.

Lithopone, a compound of zinc sulphide and barium sulphate, is a white pigment formerly made in the United Kingdom, but now imported. This material has been largely replaced by titanium dioxide. Barium titanate is important to the electronics industry because of its high dielectric constant. Barium ferrite is an important new permanent magnetic material with many uses particularly in electric motor construction.

PART I BARYTES

Terminology, properties and mode of occurrence

'Barytes' (synonyms: barite; baryte) is naturally occurring barium sulphate, $BaSO_4$, commonly known to miners as 'heavy spar' because of its high specific gravity. The term 'baryte' is generally used in the United Kingdom to denote the mineralogical species whilst 'barytes' usually refers to the commercial mineral; in the USA, 'barite' is used in both senses. In Derbyshire and Somerset a fibrous variety of baryte, occurring with lead ore, has for centuries been known as 'caulk', sometimes written 'cawk', 'cauk' or 'calk'. 'Baryta' is a term sometimes used in the trade to refer to chemically refined barium sulphate, more commonly known as 'blanc fixe', and sometimes used for the oxide. Baryte is a heavy mineral, with a specific gravity of 4.3 to 4.6. It has a hardness of 3 to 3.5 on Mohs' scale and is brittle, with two perfect cleavage directions. It is colourless or white when pure, but inclines to yellow, grey, blue, red, green, brown or dark brown according to the impurities. The lustre of coarse grained barytes is vitreous to greasy or silky, sometimes resinous or pearly, but fine grained masses frequently look earthy. Baryte forms orthorhombic crystals, commonly tabular, but sometimes prismatic. Ordinary baryte usually forms broad or stout crystals, which are sometimes very large, but sometimes slender needles. It sometimes occurs in granular masses resembling marble and in globular or nodular concretions which are generally sub-fibrous or columnar within. Stalactitic baryte from Derbyshire sometimes resembles petrified wood. Baryte decrepitates, or flies apart, when heated. Some varieties fluoresce under ultraviolet light, the colour produced varying with the impurities. Pure baryte contains 65.7 per cent of barium oxide and 34.3 per cent sulphur trioxide, but barytes frequently contains some strontium, the variety with a high strontium content being known as barytocelestite; some rare varieties are rich in lead and radium (hokutolite). Fetid barytes is so called because of the smell given off when struck, or when two pieces are rubbed together. Some calcium sulphate is frequently present as an impurity; silica, clay, bituminous and carbonaceous material are sometimes present. Pink or reddish barytes, generally containing some haematite as impurity, is a common variety.

Barytes is by far the most important of the naturally occurring barium minerals and is the most widely distributed anhydrous sulphate after anhydrite. It occurs in hydrothermal deposits in veins and beds associated with calcite, fluorite and quartz, and as a gangue mineral associated with ores of lead, copper, iron, zinc, gold, silver, nickel, cobalt, manganese, rare earths,

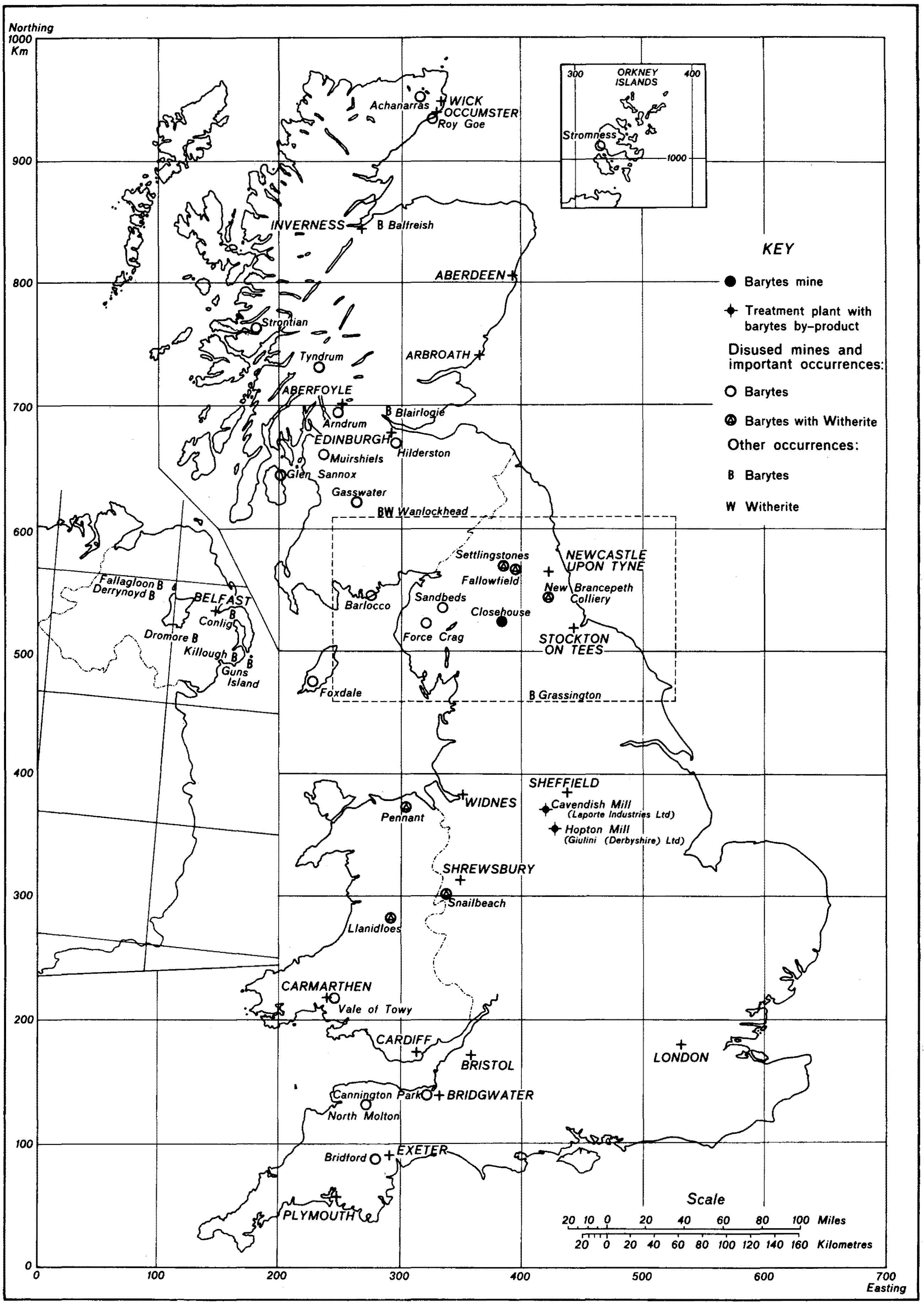

Fig 1 Location of barytes and witherite mines, major occurrences and beneficiation plants in the United Kingdom.

uranium and antimony. Less commonly it occurs in massive form associated with haematite deposits, in sedimentary deposits of manganese and sometimes as earthy masses in beds of marl. It is sometimes found as residual nodules resulting from the decay of baryte-bearing clays and limestones. Baryte forms the cementing material of some sandstones. 'Desert roses' are rosettes of plates of baryte with sand or earth inclusions. Baryte also occurs as stalagmitic, stalactitic and sinter deposits. It is chemically inert and is thus found in eluvium, often as coarse clastic material, as well as in the heavy sand residue of placer sluicing operations. It is also reported to occur on the sea bed.

Resources

England

Barytes has been worked in many parts of the United Kingdom (see Fig 1) but most of the better quality barytes occurs in the Northern Pennine orefield (Fig 2). A generally less valuable type occurs in the Peak District of Derbyshire, in the Southern Pennine orefield.

The Northern Pennine orefield, mainly high moorland country, is a fault block uplifted along its western margin and inclined gently to the east, the eastern boundary being the Durham coalfield. The area is composed of gently folded Lower Carboniferous sediments which consist of an alternating series of shales, sandstones and limestones, intruded at various horizons by sills and dykes of quartz-dolerite. Mineral veins are widespread throughout the orefield forming ribbon-shaped ore bodies, chiefly developed in the more competent members of the sequence, particularly the limestones. The major trend of productive veins is ENE with a set of more weakly mineralised fractures trending NNW. Individual fractures can be traced for distances of up to several miles, but are not always continuously mineralised. A lateral distribution of primary minerals has been noticed, fluorite and barytes being the dominant vein minerals. Veins where fluorite dominates occur towards the centre of the field; around its fringe the veins consist chiefly of barytes. There is a narrow transitional zone where both minerals occur.

At Closehouse in the North Riding of Yorkshire, chemical grade barytes is mined from a vein up to 17m wide. The main deposit is a replacement of a quartz-dolerite dyke, but a little further west large lenses of white barytes occur in shale. The workings extend about 1km underground. Athole G Allen (Stockton) Ltd, the owners of the mine which is the only surviving barytes mine in the UK, are increasing the rate of production at Closehouse and may resuscitate production and development at their Lunehead mine. Although they have a continuing latent interest in the New Brancepeth Mine, Co Durham, where the National Coal Board formerly mined both barytes and witherite, the difficulties involved in re-opening the mine are manifold.

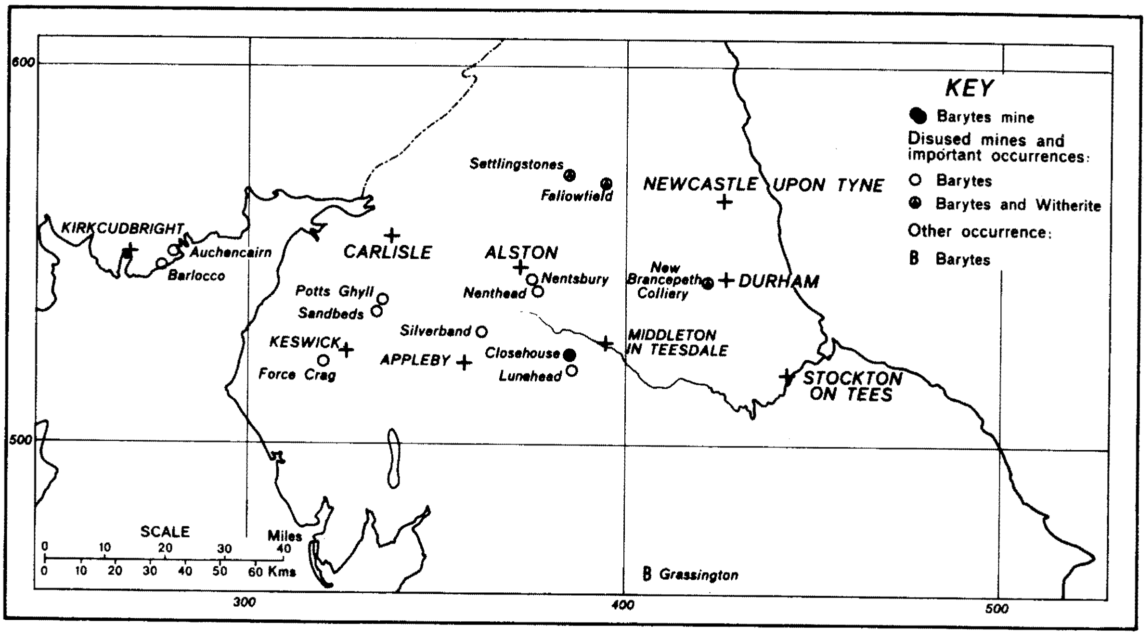

Fig 2 Location of major workings and occurrences of barium minerals in the north of England.

The Southern Pennine orefield, the old lead mining field of West Derbyshire, covers the eastern half of a massif of Carboniferous Limestone. It extends from Castleton in the north to Wirksworth and Brassington in the south. A great number of mineral veins have been worked for lead in this area. They are most prolific in the eastern margin of the massif where the limestone generally dips steeply beneath a cover of shale. Along the eastern margin, fluorite predominates as the matrix of the veins, and provides the greater part of the UK fluorspar resources and production, and an increasing quantity of by-product barytes. Further west, the proportion of fluorite decreases, and baryte often becomes the dominant mineral; in addition to normal fissure veins there are pipe-like replacement deposits, some of which are reported to have reached 50m in width, eg at the Golconda barytes mine, and thicknesses of 15m have been reported near Matlock.

In Derbyshire the Carboniferous Limestone Series consists of massive limestone with interbedded basaltic lavas, known locally as 'toadstones', and tuffs, and intruded sills and necks. Differences in solubility and permeability between limestone and lava had a profound influence on channelling the flow of ore solutions into the joints and fissures of the limestone.

The principal Derbyshire source of barytes was in the vicinity of Wirksworth. A flat worked between 1915 and 1945 at the Golconda Mine produced about 75,000 tonnes of barytes. There are large dumps, particularly those from the former Millclose Mine, which contain large quantities of generally second-grade barytes, mixed with other material.

An amorphous or earthy form of barytes known as 'caulk' occurs in quantity in parts of Derbyshire; some of this is pale in colour. The crystalline variety, known at Eyam as 'tush' is of less value, particularly when it is stained red with iron impurities. The caulk was in the past used in the manufacture of white paint, after bleaching.

Barytes occurs in varying porportions in the spoil heaps of disused lead mines in Derbyshire associated with the more abundant and valuable fluorspar. An increasing quantity of barytes is now being extracted by flotation from this material.

Barytes is fairly widespread in Lower Palaeozoic rocks in the Lake District, occurring in the Skiddaw Slates, in the surrounding Borrowdale Volcanic Series, and to a lesser degree in the adjacent Silurian and Carboniferous rocks. In the Caldbeck Fells area of the Lake District a series of veins containing non-ferrous ores, barytes and other minerals traverse Lower Palaeozoic igneous and metamorphic rocks. These veins were worked until 1966 by McKechnie Bros Ltd of Widnes in their Force Crag, Potts Ghyll and Sandbed mines. At the Force Crag Mine near Keswick the veins occur in Skiddaw Slates, while at Potts Ghyll and Sandbed mines they occur in rocks of the Borrowdale Volcanic Series. The barytes mined in the Lake District was used in lump form for the production of barium chemicals, mainly lithopone, and attempts are reviving production have been reported. Further resources of barytes are known to exist in the Silverband Mine in Westmorland which was closed in 1963.

Substantial resources of good quality barytes were proved in the south-western workings of Settlingstones witherite mine before it closed in 1969, but economic extraction was not considered feasible. Barytes occurs as a gangue mineral in veins and as widespread disseminations in the Upper Mottled Sandstone of the Bunter and the basement beds of the Keuper Sandstone at a number of localities in the West Midlands and in the long-disused copper mines at Alderley Edge and Mottram St Andrew in Cheshire, about 12 km SW of Stockport. These occurrences have never been exploited for barytes.

The principal area of barytes deposits in west Shropshire is within a radius of about 10km of the village of Shelve, 20km south-west of Shrewsbury. The veins occur in strata of Pre-Cambrian and Ordovician age, overlain to the north, west and south by Silurian and Carboniferous age rocks that are locally barren. Ordovician rocks with barytes veins also crop out around Breidden Hill, 20km west of Shewsbury, where the veins pass upwards into Silurian rocks. The main orefield, around Shelve, has been worked at intervals for lead from Roman times onwards. In this area the general strike of strata of all ages is NNE and the orefield is divided into two parts by the westerly dipping Stiperstones Quartzite which forms a prominent ridge. Barytes was mined for many years at the Huglith Mine where mainly pink barytes veins, up to 6m wide, occur in Pre-Cambrian rocks. About 295,000 tonnes of run-of-mine ore were produced before the mine was closed in 1948. It was worked by the Malehurst Barytes Co Ltd, which was taken over by Laporte Industries Limited. Small amounts of copper ore are associated with the barytes veins.

In South Devon, in the Teign Valley, veins containing barytes and associated sulphide minerals occur in Devonian and Carboniferous cherts and shales at intervals along a north-south belt some 8km in length. The Bridport Mine produced about 370,000 tonnes of barytes between 1887 when working commenced and 1958 when the mine was closed; record annual production of 21,000 tonnes was attained in 1940. This mine was also taken over, in 1950, by Laporte Industries Ltd. The barytes is associated at depth with sulphide ores, and the difficulty in obtaining pure barytes was one of the reasons for abandoning the mine. In North Devon a number of veins containing barytes are known. Some of the dumps of old copper mines, eg near North Molton, may contain enough barytes to justify reworking. In Somerset, veins of barytes up to 0.6m wide traverse Carboniferous Limestone at Cannington Park, near Bridgwater.

Barytes is a common gangue mineral of the lead-zinc ore-field of the Mendip Hills which was worked until the middle of the 19th century, before there was any large demand for barytes. No large barytes veins are known, however.

Scotland.

Barytes is a common constituent of many Scottish mineral veins, but it is often present in small quantities or is too intimately associated with impurities to be of economic value. Some veins consisting almost entirely of barytes have been worked, but there has been no production since 1969. The most important mines in Scotland (see Fig 1) were the Muirshiel Mine in Renfrewshire and the Gasswater Mine in Ayrshire which together had a combined annual production of up to 30,000 tonnes of barytes. Both were owned by the Rio Tinto-Zinc Corporation in their last years of working. Mining at Muirshiels is believed to have started in about 1750 as an opencast operation. The barytes was creamy to pink in colour and occurred as a nearly vertical vein, 2 to 5m thick, in an area of almost flat flows of greenish basalt of Calciferous Sandstone age. The iron content of the vein was reported to be increasing before the mine finally closed in 1969. The Gasswater Mine, 6.5km southwest of Muirkirk, occurs on a line of crush in the Old Red Sandstone. One of the veins worked was up to 8m thick and varied in colour from white to pink. This mine was operated at intervals during the present century, but closed in 1964. Some of the earlier operations were opencast workings, but later operations were underground down to the 154m level.

The Glen Sannox Mine (see Fig 1) in the north-east corner of the island of Arran produced about 60,000 tonnes of barytes during the present century. The country rocks are fine-grained, marly, purplish sandstones and red mudstones of Lower Old Red Sandstone age. The barytes was white to pinkish in colour and was reported to be of exceptional purity. Veins occurred up to 3.5m wide but were generally about 0.6m wide.

The Barlocco Mine in Kirkcudbrightshire (see Fig 1) is an abandoned working 11km E by S of the town of Kirkcudbright. Two nearly vertical veins of pink barytes, up to 2m wide, traverse Silurian slates. The mine was first opened before 1850 but the annual output was usually only a few hundred tonnes; it ceased to produce barytes in the 1920's. A barytes vein 0.6m wide cuts reddish grits at Auchencairn, 3km from Airds farm in Kirkcudbrightshire, and yielded about 900 tonnes of good quality barytes. Barytes also occurs in the spoil heaps of a disused copper mine lying a short distance to the west. Barytes is a common gangue mineral at the now disused lead-zinc mines at Wanlockhead, Dumfriesshire.

There are a large number of mineral veins in the Ochil Hills, some of which contain barytes, but only near Blairlogie (see Fig 1) in Stirlingshire have any of these been of economic interest. Several veins are up to about 1m in width, one widening locally to 3.5m. Some veins contain minor quantities of associated copper minerals, mainly malachite. Some active exploratory work may be justified here. White barytes in a vein about 2m wide consisting almost entirely of barytes was reported many years ago in Linlithgowshire near the abandoned Hilderston silver mine, now flooded, about 7.5km south of Linlithgow but is no longer visible. Where the vein traversed limestone, niccolite and argentiferous galena were associated with the barytes. The old limestone quarry nearby is also flooded.

Barytes has been reported to occur as layers and disseminations throughout limestone and conglomerate of Old Red Sandstone age in a disused quarry SW of Balfreish farmhouse east of Culloden Moor, Nairn. A vein of pink barytes, varying in thickness from 2.5cm to 2m, occurs in the cliff at Forbidden Cave, 5kms NE of Arbroath, Angus, cutting Old Red Sandstone rocks. There are a number of abandoned mines near Aberfoyle, Perthshire, some of which have yielded creamy or reddish barytes and small quantities of copper minerals. The barytes veins up to 1m thick cut Old Red Sandstone conglomerates and dark red mudstones associated with vesicular andesites, and have been worked by opencast mining, eg at Gartloaming. Barytes occurs in the Tyndrum mining district of Perthshire near the Argyll border, where lead has been mined at intervals since the 18th century. The primary ores are galena, sphalerite (zinc blende), chalcopyrite and pyrites. There are large dumps associated with the former workings. Pink barytes occurs as gangue in the disused Burn of Sorrow mine, Perthshire, about 1km NW of Castle Campbell, which was worked in the 18th century for lead and copper. Several veins worked for galena at the Whitesmith and the Middlehope mines near Strontian, Argyllshire, contain barytes gangue; a fair quantity of barytes is present in dumps at Bellsgrove Lodge nearby. Trials east of the Bellsgrove opencast showed that the vein consisted principally of barytes, with some galena. Consolidated Gold Fields Ltd re-examined the galena and sphalerite occurrences near Strontian, but abandoned their interest a few years ago.

Barytes occurs as nearly vertical veins in the Old Red Sandstone rocks of Caithness (see Fig 1). In some areas, eg near Wick, it is associated with lead and copper sulphides. At Roy Goe, 1.6 km SE of Occumster and 19km SSW of Wick, a vein of white barytes was worked from 1915 to 1918, with a maximum production of 1,434 tonnes in 1916. The vein measured about 1m thick in the sea cliff, increasing to 3m thick in the mine, which was worked at 3 levels. On the farm of Achanarras 3.5km SSE of Halkirk, Caithness Flags of Old Red Sandstone age are cut by a 1.5m vein with a 0.3m wide zone of dirty white barytes and 0.45m of broken stuff with galena. There was small-scale mining for a few years between about 1913 and 1918, which yielded some saleable barytes. Barytes gangue is associated with the lead ore formerly mined on a small scale 1.6km west of Stromness of the Mainland of Orkney. Barytes veins occur traversing Old Red Sandstone north-west of Stromness associated with pyrites and galena. Red stained barytes occurs on the island of Hoy associated with argentiferous lead veins.

Wales

Barytes occurs widely in Wales, (see Fig 1) chiefly as a vein mineral and often in association with lead and zinc ores. It tends to be present in the upper or outer zones of non-ferrous metalliferous ore fields. Veins containing barytes have been worked in North and mid-Wales and in Carmarthenshire, and in the Carboniferous Limestone of north-east Wales, and the south-eastern rim of the South Wales coalfield. In the Vale of Glamorgan barytes veins occur which cut Mesozoic beds. Between 1854 and 1939 a total of 75,062 tonnes of barytes was produced in Wales. In the heyday of lead mining, barytes was largely discarded, and some old mines may repay investigation for occurrences of barium minerals.

Some minor production of barytes was recorded in 1971 from near the old Vale of Towy mine (Nant Shaft) which is located 2.5km east of Carmarthen. A 1m vein of white barytes was found to peter out at depths of 60m below the surface. It appeared to be replaced by a lode containing mixed sulphides. Barytes is also present at Gelli-Deg near Llandyfaelog, about 10km to the south of Carmarthen. In the western half of the Vale of Glamorgan thin veins and associated concretionary swellings of barytes are of fairly common occurrence in the Carboniferous Limestone and also in limestones and limestone conglomerates or breccias of Triassic and Lower Liassic age. Barytes veins, locally up to about 1m thick, are also particularly conspicuous in quarry exposures of the dolomites (Carboniferous Limestone) of south-east Glamorgan and the adjoining area of southern Monmouthshire. In eastern Montgomeryshire a recent expansion in a southerly direction of the large Criggion quarry, working the dolerites of the Breiddon Hills, has encountered notable occurrences of barytes in vein form.

Northern Ireland

Although there has been little barytes production in Northern Ireland, veins containing barytes have been reported to occur in all six counties (see Fig 1) frequently associated with lead and sometimes copper in small quantities. Some of the veins may be worth further investigation, but no economic deposits have yet been discovered.

Veins of barytes up to 0.4m wide are known in the Carboniferous, Old Red Sandstone and Dalradian rocks of Co Fermanagh. Barytes occurs in joints and fissures in Dalradian schists in the north of Co Antrim, eg near Ballinloughan, Tureagh and Falmacrilly, but no production has ever been recorded. At Creggan Duff in Co Armagh a lode of galena and pyrite with barytes gangue traverses Silurian slates and grits. Some lead ore was extracted here at one time. In Co Down there are several localities where base metal lodes cutting Silurian slates contain barytes gangue. At Conlig and Whitespots, about 1km north of Newtownards, a lode with galena was mined during the first half of the 19th century. Barytes occurs in the gangue, and small quantities of copper ore are also present. In the south of Guns Island, 5km NE of Ardglass, close to the mainland, small barytes veins with associated copper and lead have been reported as cutting Ordovician rocks. At Rathmullan Upper a lode formerly mined for lead at Glebe House is reported to contain barytes and gypsum gangue. Due south of the village of Killough, narrow barytes veins are reported cutting Silurian rocks. There are slight traces of copper and iron pyrites associated with a nearby basalt dyke visible only at low water. In the vicinity of Dromore, barytes associated with lead has been reported in veins cutting Ordovician rocks.

In Co Londonderry small amounts of barytes occur at a number of localities. About 1.6km due west of Draperstown a small vein of good quality white barytes cuts Calciferous Sandstone and outcrops on the right bank of the Moyola river. Alluvial gold has been found in very small quantities nearby. At Derrynoyd, also in Calciferous Sandstone, there was a small barytes mine; the barytes on the associated spoil heap is red-stained. A 1.5m wide vein of barytes with red ferruginous material occurs 180m NNW of Carncose Rock. Minor barytes veins, cutting metamorphic rocks and Old Red Sandstone conglomerates, are also known in Co Tyrone, although there are few available details. The Old Red Sandstone is often cemented with barytes.

Isle of Man

Barytes occurs as a gangue mineral associated with argentiferous galena veins which were mined many years ago in the Foxdale area of the Isle of Man. The barytes was then of no value and it is possible that some barytes may remain in the old mines.

Land use

Barytes is mainly won by underground mining, which does not normally affect the land surface to any appreciable extent. In the Northern Pennines and the Lake District the total area of permissions under the Town and Country Planning Acts for the mining of all vein minerals is about 100,000 acres (405 sq km). Similar permissions granted in the Southern Pennines, mainly for underground working, cover about 7,000 acres (28 sq km).

Older workings in some of the mineralized veins, originally for metalliferous ores, with barytes or witherite discarded as waste, have given rise to localised subsidence, and could still continue to do so in the future, but modern underground workings are unlikely to give rise to subsidence.

Some barytes is, or has been, won from the waste tips from former lead-zinc mines, such as those near Nenthead, Cumberland, Grassington Moor, West Yorkshire and Longstone Edge, Derbyshire. Where an old tip retains its original appearance as a heap of waste material deposited on the ground, it is treated as a chattel (ie movable possession) and hence planning permission for working it is not required. The working of naturalised tips does however require planning permission, to which appropriate restoration conditions can be attached. Unless carefully controlled, reworking of old waste tips can be detrimental to the appearance and possibly to the agricultural quality of the land.

The Northern Pennine areas of barytes extraction are in sparsely populated uplands of negligible agricultural value. They are within designated 'Areas of Great Landscape Value', but although there is some disturbance of amenity due to mine buildings, processing plant and waste tips, the effect in these areas is small. Much of the Southern Pennine orefield, where Laporte Industries Ltd produce barytes as a by-product of fluorspar extraction, is within the Peak District National Park. Here there have been some amenity objections, mainly because of the spoil heaps and settling lagoons associated with the processing plant.

Industrial uses and specifications

Ground barytes is used principally because it is heavy, chemically inert and relatively cheap. Its main use is in finely ground form (passing 325 mesh US standard sieves) as a weighting agent in the muds circulated in the rotary drilling of oil and gas wells. These muds lubricate the drill and the stem, seal off and support the walls of the hole, remove cuttings, and help to confine the high oil and gas pressures met at depth, preventing caving and blowouts. The barytes used in heavy drilling muds is now probably nearly half the total consumption in the United Kingdom for all purposes, whereas about 79 per cent of all barytes consumed in the USA in 1970 went into drilling muds. The demand for barytes is thus a function of oil and gas well drilling activities and fluctuates accordingly. The type of barytes used in oil well drilling muds can be somewhat less pure than that required for many other purposes.

The colour is not important but the specific gravity of the material must not be below 4.2 and the iron content must be relatively low. The details are given in specification No DPP - 3 (1959) revised 1963 prepared by the Drilling Mud Additives and Oil Well Cement Panel of the Oil Companies Materials Association, London. The barytes concentrates now being produced in increasing quantities as an end-stage flotation by-product of fluorspar extraction in Derbyshire are suitable, after processing, for heavy drilling muds.

Much of the remainder of the world's barytes production goes into the manufacture of glass, as a flux, and to add brilliance and clarity; into paint as an extender, into rubber as a filler and to the chemical industry for the preparation of barium compounds (see Part III). Nearly half the United Kingdom barytes requirements are for chemical production, for which purpose imported ore is now mainly used. Barytes is a common industrial filler, extender and weighting agent. It is added to bristolboard, playing cards, heavy printing papers, rope finishes, brake linings, clutch facings and plastics.

The paint and allied trades consume the largest tonnage of white barytes, principally in primers or undercoats. Barytes in paint produces a tight, dense film with good corrosion resistance, particularly important in motor car manufacture which takes about one-third of all the paint grade barytes. Micronised grades are now replacing blanc fixe (see Part III) which is more expensive and has higher oil absorption.

The limits of composition and properties of barytes for use as an extender in paints are given in BS 1795: 1965. Barytes for use in paints is also described in Admiralty (CINO) specification No K 1290 and there is a War Office C.S & T.S. specification for lead-free barytes, No 984C. The chemical inertness of barytes makes it useful in some chemically resistant coatings. All grades of barytes are characterised by very low oil absorption. Barytes low in iron and lead is used in the continuous tank glass manufacturing process, where a minimum of 98 per cent $BaSO_4$ is usually required. The barytes dissolves in soda ash to form a heavy liquid which sinks to the bottom of the tank; here it reacts with silica to form sulphur dioxide and oxygen which stir the melt and remove occluded gases. No barytes produced at present in the United Kingdom is regarded as good enough for this purpose. For the manufacture of optical glass the strontium impurity content of the barytes, or of the chemicals derived from it, is of importance. Barytes forms about 50 per cent of the ceramic body used by Wedgwood in their 'Jasper' ware, a refined type of ornamental stoneware. Imported ore of a good white colour, eg from India or China, is used for this purpose.

Because barytes absorbs gamma radiation well, its use reduces the amount of expensive lead shielding which would otherwise be necessary. For shielding purposes, eg in nuclear reactors and hospitals, it is used as gravel-sized lumps in aggregate for special concrete, and in bricks. It is also used in heavy aggregate for concrete where extra weight is required, eg to keep pipelines buried in swampy ground.

A mixture of synthetic rubber powder and finely ground barytes has been combined with hot asphalt for roads, airport runways and parking places to produce a tight, flexible sealing coat that prolongs the life of a road surface. Barytes is used in coal preparation (Barvois system), but many of the older British collieries which used this system have been closed in recent years and the newer collieries use a different system which does not require barytes.

In sand blasting, a relatively hard variety of barytes is used, prepared from UK ore. Barytes is used as a filler in soft rubber products, eg insulating tapes, and in backings, eg in foam rubber carpet backings. Another minor use for UK barytes is as one of the components of the cores of golf balls. Barytes has long been used for weighting textiles.

For use in barium chemical manufacture the fluorine content of the feedstock is important. Where 1.5 to 3 per cent of calcium fluoride is present as a contaminant the material is unsuitable. Crude barytes for the preparation of barium chemicals by reduction in the United Kingdom should contain at least 92 per cent of barium plus strontium sulphates; the silica content must be less than 4 per cent, the calcium carbonate less than 2 per cent and there must be less than 1 per cent of ferric oxide, alumina and calcium fluoride with less than half a per cent of lead. The material must be granular or lumpy. Crude barytes required for bleaching purposes has to fulfil somewhat similar requirements except that the basic colour must be white, coloured impurities being permitted only if they can be released by fine grinding.

Price and cost

UK barytes is produced in different grain sizes. Subsequent upon a price increase effective in August 1971, the average price in January 1972 appears to be about £10/£11 per tonne delivered for crude, dressed, chemical grade concentrates, minimum 92 per cent $BaSO_4$.

The following prices of imported barytes have been quoted as being current for January 1972:

Imported, ground, white, paint grade, 96–98 per cent $BaSO_4$, 99 per cent 240 mesh, 10 tonne lots delivered UK:	£40 per tonne
Micronised, minimum 99 per cent finer than 20 microns, delivered UK:	£51 per tonne
Imported, lump, unground, 90–98 per cent $BaSO_4$, bulk, CIF:	£8 to £11 per tonne
Moroccan, drilling mud grade, ground, S.G. 4.2, CIF delivery point:	£12 to £14 per tonne

The cost of transporting barytes, particularly by rail or road, is high in relation to its selling price.

Technology

The character and intended use of the ore govern the processing, some of which is usually performed close to the mine. For some purposes crushing, washing, size grading into lump, sand and fines and drying are necessary. For other uses, beneficiation by flotation or acid bleaching are required. Some barytes, known as 'micronised', is milled to fine tolerances with particle sizes of less than 5 to 20 microns. Some imported material referred to as micronised, is in fact only classified and has not actually been micronised. For some purposes the grain size distribution of classified barytes is inferior to that of the truly micronised barytes. Barytes used for the paint and allied trades is crushed and ground, wet or dry, to produce varying grades based on particle size distribution.

Production

Barytes production in the United Kingdom totalled about 4 million tonnes between 1854, when official records were first published , and 1970 (see Fig 3). The annual rate of output increased from about 20,000 tonnes at the turn of the century to over 60,000 tonnes by the 1930's and reached a peak of 113,000 tonnes in 1940. A high level of some 90,000 tonnes a year was maintained throughout the Second World War and the immediate post-war period when overseas supplies were severely restricted. This was followed by a gradual decline during the 1950's and early 1960's followed by a sharper fall to only 24,000 tonnes in 1969 and an estimated 21,000 tonnes in 1970.

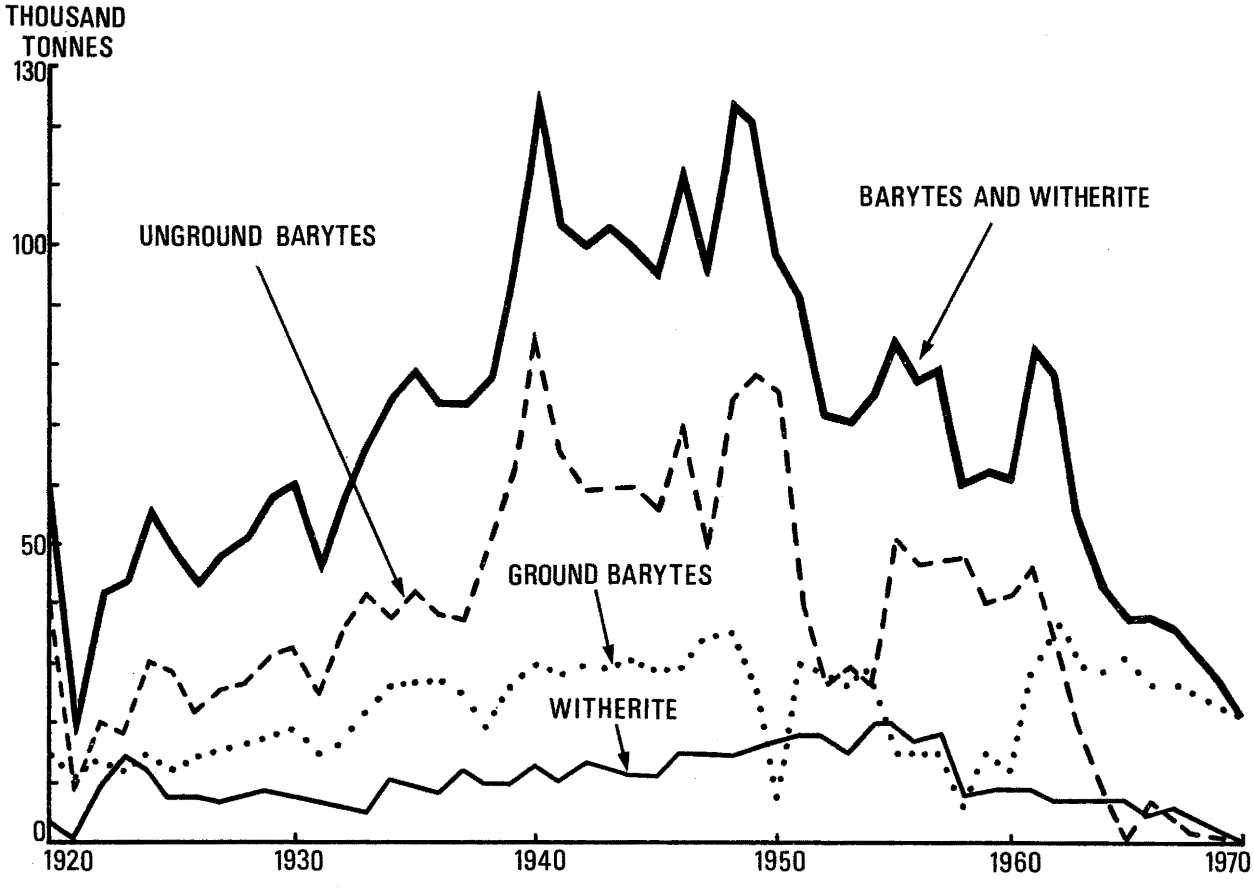

Fig 3 Production of barytes and witherite in the United Kingdom from 1920 to 1970.

For some years an increasing quantity of barytes has become available as a by-product of fluorspar production in Derbyshire, and a further increase is expected to occur in 1972.

Table 1 United Kingdom: Production of barytes and witherite, 1854–1970

Thousand tonnes

Period	*Barytes*	*Witherite*	*Barytes and witherite*
1854 – 1860	78	12	90
1861 – 1870	51	31	82
1871 – 1880	85	42	127
1881 – 1890	113	69	182
1891 – 1900	112	72	184
1901 – 1910	228	76	304
1911 – 1920	414	64	478
1921 – 1930	387	84	471
1931 – 1940	681	93	774
1941 – 1950	913	135	1,048
1951 – 1960	575	152	727
1961 – 1970	389	55	444
Total, 117 years 1854 – 1970	4,026	885	4,911

Sources:

1854 – 1919: Ministry of Fuel and Power, Report of the Mineral Development Committee (Westwood), Cmd 7732, 1949.

1920 – 1938: Mines Department, Annual Reports.

1939 – 1947: Ministry of Fuel and Power, Annual Digest of Statistics.

1948 – 1969: Department of Trade and Industry records (partly unpublished)

1970: IGS estimate.

A breakdown of this production from 1854 to 1939 on a district and county basis is shown in Table 2.

Table 2 Great Britain: Details of barytes production, 1854–1939

Thousand tonnes

District	*County*	*Country rock*	*Production*
Northern Pennines (Northern Area)	Northumberland	Carboniferous Limestone Series	*(a)*
	Cumberland		4
	Durham		78
	Westmorland		61
	Yorkshire		80
Durham Coalfield	Durham	Coal Measures	123
Northern Pennines (Southern Area) and Central Pennines	Yorkshire	Carboniferous Limestone Series	45
Southern Pennines	Derbyshire		269
Lake District	Cumberland	Ordovician	35
Shropshire and Wales	Shropshire	Pre-Cambrian-Ordovician	589
	Flintshire	Silurian	11
	Montgomeryshire		67
	Denbighshire		*(a)*
South West England	Devon	Culm	227
	Cornwall		*(a)*
	Somerset	Carboniferous	6

Total:	England and Wales	1,596
	Scotland *(b)*	405
	Great Britain	2,001

(a) Small production only; approximately 400 tonnes in Northumberland, 500 tonnes in Denbighshire and 5 tonnes in Cornwall.

(b) Chiefly Ayrshire (Gasswater) and Bute (Glen Sannox); some production in Renfrewshire, Kirkcudbrightshire, Perthshire, Lanarkshire and Caithness.

Sources: K C Dunham, *Trans IMM,* Vol LIII, 1944.
Barium Minerals in England and Wales. GS & M Wartime Pamphlet No 46, 1945.
Barium Minerals (2nd edition), 1937. Mineral Resources Department, Imperial Institute.

In the period since 1939 no precise details of barytes production by district or counties have been published. National production, year by year, has been as follows.

Table 3 United Kingdom: Production of barytes, 1940–1970*

Thousand tonnes

Year	*Unground*	*Ground*	*Total*
1940	84	29	113
1941	65	28	93
1942	58	29	87
1943	59	29	88
1944	59	30	89
1945	55	29	84
1946	69	29	98
1947	47	34	81
1948	74	35	109
1949	78	25	103
1950	75	6	81
1951	41	30	71
1952	26	27	53
1953	29	26	55
1954	26	28	54
1955	50	14	64
1956	46	14	60
1957	47	14	61
1958	47	5	52
1959	39	14	53
1960	41	11	52
1961	46	28	74
1962	34	36	70
1963	18	29	47
1964	7	28	35
1965	–	30	30
1966	6	26	32
1967	4	26	30
1968	1	25	26
1969	1	23	24
1970	1	20	21

*** Official production records generally available only to the nearest 1,000 tonnes.**

Sources: 1940–1947: Ministry of Fuel and Power, Annual Digest of Statistics.

1948–1969: Department of Trade and Industry records (partly unpublished).

1970: IGS estimate.

Overseas trade and consumption

Imports

The United Kingdom is no longer self-sufficient in barytes, and in 1970 over three-quarters of the domestic requirements were imported at a cost of nearly £700,000. The use of barytes in drilling muds during exploration for natural gas and oil in the North Sea has led to a marked increase in the imports of barytes in recent years. Most of the UK imports of barytes is unground ore, now mainly from Morocco, as shown in Table 5. In 1972 the rate of import duty was 5 per cent, but imports from Commonwealth and EFTA countries were free of duty. Between 1919 and 1939 imports averaged about 38,000 tonnes a year. Annual imports since then are shown in Table 4. The imports of ground and unground barytes into the UK from 1920 to 1970 are shown in Fig 4.

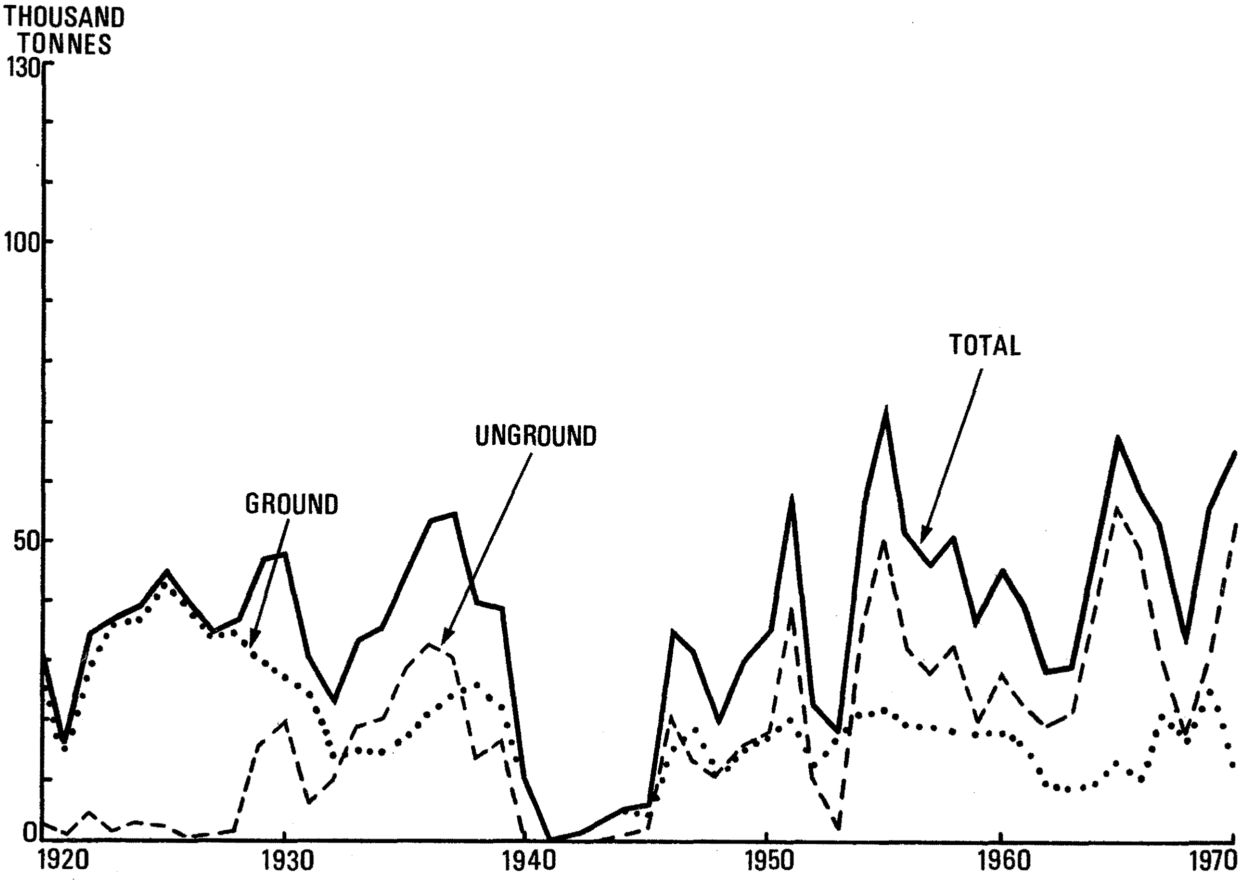

Fig 4 Imports of ground and unground barytes into the United Kingdom from 1920 to 1970.

Table 4 **United Kingdom: Imports of barytes, 1940–1970**

Year	*Unground*	*Ground*	*Total*	
	Tonnes		*Tonnes*	*C.i.f. Value* £
1940	181	10,754	10,935	74,973
1941	–	1	1	*n.a.*
1942	–	578	578	5,826
1943	97	2,662	2,759	26,948
1944	305	4,373	4,678	43,071
1945	1,720	4,032	5,752	46,561
1946	19,934	15,301	35,235	264,765
1947	13,436	17,957	31,393	294,784
1948	10,294	10,093	20,387	159,062
1949	15,213	14,616	29,829	223,070
1950	17,669	17,799	35,468	267,324
1951	39,294	19,936	59,230	486,724
1952	11,933	11,334	23,267	219,652
1953	2,382	16,299	18,681	226,728
1954	34,607	21,555	56,162	464,281
1955	50,937	22,167	73,104	609,598
1956	31,910	19,336	51,246	481,642
1957	27,515	18,941	46,456	494,345
1958	32,626	18,135	50,761	524,175
1959	19,364	18,087	37,451	430,702
1960	28,084	18,371	46,455	507,661
1961	23,176	15,477	38,653	409,740
1962	19,331	8,515	27,896	284,803
1963	21,024	7,458	28,482	285,871
1964	38,393	8,963	47,356	442,474
1965	55,355	12,800	68,155	592,656
1966	47,856	9,947	57,803	514,978
1967	31,139	20,857	51,996	538,865
1968	18,161	15,744	33,905	450,074
1969	31,256	25,242	56,498	682,253
1970	54,136	11,528	65,664	684,912

n.a. information not available.

Source: HM Customs and Excise, Annual Statement of Trade.

Table 5 United Kingdom: Imports of barytes, 1969–1970, by countries of consignment

Description	*Quantity imported tonnes*		*C.i.f. value £*		*Average c.i.f. value £ per tonne*	
	1969	*1970*	*1969*	*1970*	*1969*	*1970*
Unground						
from Morocco	14,828	23,327	117,498	189,698	8	8
Spain	8,929	15,512	73,958	134,932	8	9
Italy	7,150	14,071	63,270	117,128	9	8
Irish Republic	813			6,952		9
Turkey	20	206	229	3,383	11	16
China		200		2,636		13
USA	10	6	772	494	77	82
West Germany	315		5,563		18	
France	3		146		49	
Total	31,255	54,136	261,436	455,223	8	8
Ground						
from Irish Republic	6,656	5,062	105,629	79,655	16	16
Morocco	7,585	2,599	89,386	36,242	12	14
West Germany	4,623	1,607	108,058	54,563	23	34
China	2,461	1,472	46,672	29,825	19	20
Netherlands	674	544	17,526	13,757	26	25
France	42	155	1,534	5,266	37	34
Canada		27		5,073		188
USA	25	23	1,875	4,090	75	178
India		20		427		21
Spain	1,619	10	24,546	193	15	19
Belgium		7		596		85
Italy	1,552		25,463		16	
Denmark	5		128		26	
Total	25,242	11,528	420,817	229,689	17	20

Source: HM Customs and Excise. Annual Statement of Trade.

Import statistics are recorded under the following heading in HM Customs and Excise Tariff and Overseas Trade Classification:

25.11 Natural barium sulphate (barytes); natural barium carbonate (witherite); whether or not calcined:

Unground . . . . Code No 2511 0006
Ground . . . . Code No 2511 0052

It is unlikely that any witherite is imported into the UK.

Exports

There have been almost no exports of crude barytes from the United Kingdom for many years. There are small exports of ground barytes, mainly to the associates of British paint and rubber companies overseas. Small quantities of processed ore have been exported for radiation shielding purposes in hospital construction.

Consumption

Official statistics on barytes consumed in the United Kingdom are not available. Apparent consumption (ie production plus imports less exports) has fluctuated from about 137,000 tonnes in 1955 when lithopone production was in full swing to only about 60,000 tonnes in 1968, before barium carbonate requirements for television glass began to increase. Consumption of unground ore has generally been much larger than that of the ground ore, sometimes nearly three times as great, but in 1968 more than double the quantity of ground ore was consumed than unground. Consumption of ground barytes for oil and gas well drilling muds, particularly on the Continental Shelf, has increased in recent years and seems likely to increase further as a consequence of drilling in the northern part of the North Sea. This requirement has been met in part by imports from Morocco and elsewhere, and in part by English production, mainly by-product barytes from fluorite operations in Derbyshire.

Demand trends

There has been an increased demand for barytes during 1971 due mainly to an increase in requirements for use as a weighting agent in drilling muds for oil and gas exploration and development, particularly in the North Sea. In 1967 imports of ground barytes rose by 112 per cent on 1966, and continued at a high level up to 1969, but fell in 1970 as greater quantities of by-product barytes became available from Derbyshire. Imports of ground barytes from Morocco fell from 7,585 tonnes in 1969 to only 2,599 tonnes in 1970, but imports of unground Moroccan ore rose from 14,828 tonnes in 1969 to 23,327 tonnes in 1970. Imports of ground and unground barytes from Spain and Italy followed a similar pattern. Although there was a very marked change in the proportion of ground to unground ore imported, the total value changed very little from 1969 to 1970. Barytes is a multi-use mineral, and as such, decreases in some users requirements may be masked by compensating rises in other fields.

The partial replacement of white lead paint by lithopone in the 1950's led to an increase in demand for chemical grade barytes which continued for about ten years, after which lithopone was itself largely replaced by titanium dioxide. A few years later there was a rise in requirements of barium carbonate for use in television glass as a protective barrier. The recent replacement of barium by strontium in glass for colour television tubes has curtailed the US barium carbonate requirements but, so far as has been ascertained, there are no signs of any immediate change-over in the United Kingdom.

The closing down of the Settlingstones witherite mine in 1969 led to an increase in requirements for chemically prepared barium carbonate, and thus to an increase in UK consumption of chemical grade barytes for this process.

Barytes was formerly used in the manufacture of inlaid linoleum but modern types of linoleum are not inlaid and do not include barytes in their composition.

In coal washing the National Coal Board intends to change entirely from barytes to magnetite as a processing material within the next five years thus closing this minor outlet.

Many old-established uses for barytes have remained more or less static or only increased slightly in the last ten years, while others have declined; some newer uses have grown rather rapidly only to fade away after a few years. Forecasting demand for barytes is hindered by the non-availability of comprehensive end-use statistics, but is closely related to the pace of exploration for petroleum. Despite major short term fluctuations, common to the world barytes market, future consumption may continue to rise.

Substitutes

The greater opacity and much higher covering power of titanium dioxide are factors that have led to it very largely replacing lithopone in paints. The increasing availability of titanium dioxide at more competitive prices also favours substitution. For some purposes titanium dioxide is a technically acceptable substitute for both barytes and lithopone. Dolomite has been used as a substitute for white barytes because of its good colour and readier availability but for some paints the high carbonate content imparted by using dolomite is an adverse factor. For use as a filler, gypsum, anhydrite and kaolin are sometimes acceptable as substitutes for barytes, although the lower abrasion resistance imparted by kaolin as a filler in paints limits its use. Magnetite is used instead of barytes in the newer National Coal Board coal washing plants. The relatively low cost of barytes precludes the substitution of other materials in heavy drilling muds, its main use.

Industry

Athole G Allen (Stockton) Ltd own the Closehouse Mine in the North Riding of Yorkshire, the only surviving mine in the United Kingdom producing exclusively barytes, and the only UK source of chemical-grade ore. Lump ore is crushed and ground to customers' requirements at Closehouse and at Stockton-on-Tees. The company intends to increase production at Closehouse and are investigating the possibility of re-opening their nearby Lunehead Mine, which produced about 70,000 tonnes of barytes between 1884 and 1937. Prospects appear to be good in old and virgin ground, but there are serious water drainage problems. Most of the output from Closehouse is sold to Barium Chemicals Ltd, at Widnes, but some ore in processed for other customers, eg special material for radiation shielding purposes, in lump and in brick form.

Laporte Industries Ltd produce barytes concentrates at their Cavendish Mill near Stoney Middleton in Derbyshire. So far this material has been unsuitable for most chemical purposes because it is too finely ground to be amenable to transformation into the sulphide by reduction with coal or coke (see Part III), a process which requires lump ore. About half the feed for the Cavendish Mill comes from the company's underground workings at Ladywash and Sallet Hole mines, the rest from other sources, which include opencast workings and tailings dumps. The barytes is not the major object of the flotation process, and there is little incentive at present to produce material with more than 94 per cent $BaSO_4$. The 1971 rate of barytes concentrate production was about 10,000 tonnes a year which may rise in 1972 to between 13,000 and 15,000 tonnes.

Hopton Mining Co Ltd of Brassington, near Matlock, Derbyshire who specialise in the production of fine ground barytes for the paint and allied trades, are the largest UK processors of barytes. They process all the barytes flotation concentrates produced at the Cavendish Mill by Laporte Industries Ltd near Stoney Middleton, as well as some local supplies, and they also import subsidiary quantities, chiefly of white barytes for the paint industry. They clean and wash the ore from tributors.

C E Giulini (Derbyshire) Ltd, a subsidiary of an Italian mineral producer operating in Sardinia, have established a mill at Hopton, 6km south-west of Matlock, Derbyshire primarily to produce fluorspar, but with a barytes by-product due to become available towards the middle of 1972. The feed for the new mill will be derived from tributors, and from the extensive tailings at the old Millclose Mine.

Heavy drilling muds are sold for oil and gas well drilling by a small number of international companies, who make their special mixes and sell specialised services. The largest is the Dresser Magcobar division of Dresser Industries Inc of Houston, Texas, who supply the United Kingdom via the Magcobar Division of Dresser Europe SA of Brussels who have a London office. An Irish subsidiary of the same group, Magcobar (Ireland) Ltd, mines barytes on a large scale near Silvermines, Co Limerick. Baroid (UK) Ltd, a subsidiary of the Baroid Division of the National Lead Co of New York obtains some barytes from UK sources; British Ceca Co Ltd uses some Derbyshire barytes in drilling muds.

The only Scottish barytes mines active in recent years, Muirshiels and Gasswater, were both owned by a Rio Tinto-Zinc Corporation subsidiary; Muirshiels in Renfrewshire was closed in 1969 and Gasswater in Ayrshire closed in 1964. Barium Chemicals Ltd of Widnes was formed in 1964 by RTZ (Britain) Ltd and Laporte Industries Ltd on a 50:50 basis (see Part III).

McKechnie Chemicals Ltd, also of Widnes, closed their Force Crag Mine, Cumberland, in 1967 and their Caldbeck Fell mines between 1962-1965. The output was used in the manufacture of lithopone, the production of which ceased in 1969 (see Part III).

The UK barytes extraction industry has been in decline for a number of years and there has not been a great effort in recent years to find new reserves. This is partly because of the availability of cheap imported barytes, and partly because capital could obtain a better return elsewhere.

The form of most UK barytes deposits, necessitating underground working, has not permitted advantage to be taken of cost-reducing mining techniques associated with large scale opencast workings overseas. For example, Gasswater Mine, which was the largest producer until its closure in 1964, reached a maximum output of 20,000 to 23,000 tonnes per annum, compared for example with 100,000 tonnes per annum at Sidi Hammad, Morocco. Mining research has, so far, been largely ineffective in devising techniques which would lead to a substantial reduction of the cost of mining barytes underground in characteristic geological setting of UK barytes mineralisation. The low profit margin in the past discouraged the mining of barytes as such in the UK. Barytes mines may have been abandoned in Scotland at relatively shallow depth because the extraction of a low-priced mineral did not warrant further capital investment. It is possible that barytes production may increase as a by-product of the mining of fluorspar, but this type of barytes is not at present suitable for chemical manufacture.

The lack of consistency of supply, both in quality and quantity, has caused British consumers to depend to an ever-increasing extent upon imports over the last five years. The overseas supply position is easier than ever for some grades, but costs are rising, due mainly to UK handling charges, and some grades are now in shorter supply than formerly.

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PART II. WITHERITE AND OTHER MINOR BARIUM RESOURCES

Definition and mode of occurrence

Witherite is naturally occurring barium carbonate, $BaCO_3$, which when pure contains 77.7 per cent barium oxide and 22.3 per cent carbon dioxide. It is named after Dr W Withering who first described the mineral in 1784. Witherite forms orthorhombic crystals which are repeatedly twinned to form pseudohexagonal bipyramids. It also occurs in globular or reniform masses, and as granular, columnar or botryoidal aggregates. It is translucent, greyish or yellowish or almost white in colour. It is brittle, showing an uneven fracture surface with a greasy appearance, and there is one cleavage direction. The hardness is 3 to 3.5 on Mohs' scale, the same as barytes. The specific gravity is 4.3, less than barytes. Witherite is readily soluble in cold dilute hydrochloric acid. The dust of witherite is toxic to man when ingested.

Witherite is a relatively low-temperature mineral, usually occurring in hydrothermal deposits in association with calcite, dolomite, sulphides of lead, zinc and iron, and often with baryte. It is most frequently found in veins containing galena (lead sulphide) but sometimes occurs as veins in coal. Witherite commonly contains small amounts of strontium and calcium. *Barytocalcite,* $CaBa(CO_3)_2$, is a monoclinic double carbonate of barium and calcium which is relatively rare and of very little commercial value; *alstonite,* $CaBa(CO_3)_2$, is an orthorhombic mineral isomorphous with witherite of similar chemical composition to barytocalcite; and *celsian,* $BaAl_2Si_2O_8$, is similar to anorthite feldspar but contains barium instead of calcium. Barytocaclite and alstonite occur associated with witherite in the northern England.

Resources

Accumulations of witherite are extremely rare and for more than a hundred years the main world supplies of witherite were obtained from north-east England, where relatively large deposits of exceptional purity were mined from 1846 until 1969. Witherite occurrences in Wales and Shropshire have been worked in the past on a much smaller scale. Witherite is a very rare mineral in Scotland and has not been recorded in Northern Ireland.

The main occurrences of witherite are in Northumberland and Durham. The Settlingstones Mine, 10 km north-west of Hexham, Northumberland, was for many years the largest producer in the world. Production began in 1872 on the site of an old lead mine which had been in operation since 1690. An almost vertical NE-SW vein cuts Carboniferous sediments and dolerites of the Whin Sill and showed mineralization of two types. The north-easterly oreshoot, which was 1m wide, carried galena in a matrix of baryte, with a little witherite, while a second oreshoot was composed solely of witherite and had a width of 2.5 to 3m, exceptionally reaching 9m. The productive zone was 1,300m in length and occurred mainly where the vein cut the Whin Sill. The exhaustion of this exceptionally rich oreshoot of almost pure witherite led to the abandonment of the mine in 1969. Production of lead ore had ceased in 1873, soon after witherite working commenced.

The Fallowfield Mine, which ceased production in 1914, is 4 km from Hexham; the extensive workings extended 2.5 km north-east from the shaft. Between 1855 and 1912, a total of just over 100,000 tonnes of witherite was produced as well as over 11,000 tonnes of lead concentrates containing 73 per cent lead and 123 grammes of silver per tonne of lead. The vein occurs in a strong fault and in addition to witherite and galena contains some barytocalcite. Some coal was also extracted whilst the mine was in operation. Witherite is reported to occur along a fault in the nearby Acomb Colliery which was abandoned owing to an explosion in 1872. Witherite also occurs in old mine dumps in the West Allen and Wellhope area of Northumberland, and small reserves may still remain in subsurface oreshoots neglected by the old lead miners. Witherite has been reported to be fairly abundant in the dump of the Longcleugh Mine which was recently re-examined with negative results.

Witherite occurs in vein oreshoots in faults in seven different collieries in the Durham Coalfield, some of which also contain barytes. It was first discovered in 1928 in coal workings at the Morrison Colliery, then owned by the Holmside and South Moor Collieries Ltd (also known as Morrison North Pit and including the older Louis and Craighead collieries) near the village of Annfield Plain. The witherite deposit was 3 km from the colliery shafts at Morrison pit, the nearest shaft being at Burnhope Colliery 19km south of Newcastle upon Tyne. There were five witherite veins, which varied in thickness from 0.1m to 6.5m with considerable stretches 1.3m to 1.6m wide. They were remarkable in containing nearly pure witherite and only insignificant quantities of other minerals. The inclinations of the veins varied from 75 to 80 degrees. Witherite production commenced in 1932 and up to 1944 the company produced 56,773 tonnes of witherite including some from two smaller deposits in Craighead Colliery. Extraction continued until 1956 and the mine finally closed in 1958. The mine, known locally as South Moor Colliery, was taken over by the National Coal Board which continued to mine the witherite until 1956. The colliery was closed in 1958 when the economically workable reserves of coal were exhausted. Athole G Allen (Stockton) Ltd have investigated the possibility of gaining access to the remaining witherite, which is frustrated by practical difficulties, including the flooding of the colliery. The Ushaw Moor Colliery half a mile west of the village of Ushaw Moor, Co Durham, produced about 19,000 tonnes of witherite between 1922 and 1931. The deposits are no longer accessible. The New Brancepeth Colliery, Co Durham, which produced about 1,000 tonnes of witherite between 1904 and 1921, was re-opened in 1938 but was finally closed and abandoned in 1955. The witherite formed a narrow selvage to an oreshoot which consisted mainly of barytes, the main barium mineral produced.

The Nentsberry Mine, about 1.5km from Nenthead by Alston, Cumberland, produced 1,600 tonnes of witherite between 1894 and 1916. The mine also produced galena and a mixture of sphalerite and witherite which could not be separated by gravity methods. Some 2,000 tonnes of the zinc-witherite middlings produced were sold to Athole G Allen (Stockton) Ltd between 1894 and 1916 for barium chloride production.

The Lunehead Mine, 14.5 km SSW of Middleton in Teesdale, Yorkshire, which was formerly worked mainly for lead, produced barytes between 1884 and 1937 together with some witherite. Some witherite was again extracted in 1963. The witherite possibilities have been re-investigated by Athole G Allen (Stockton) Ltd since the closure of the Settlingstones Mine. Some witherite, partly converted to barytes, occurs at the abandoned Grasshill Mine 19 km north-west of Middleton in Teesdale, and at the old Cowgreen Mine now submerged under the Cowgreen reservoir. Witherite was associated with barytes at the Snailbeach lead mine nearly 3 km south of Minsterley, Shropshire. A total production of 956 tonnes of witherite was reported between 1864 and 1873.

There has in the past been a small production of witherite from two areas in *Wales*. The disused Pennant Mine at Rhuallt, 5 km east of St Asaph, Flintshire, produced 167 tonnes of witherite between 1876 and 1891, and 247 tonnes between 1913 and 1919. The principal vein, mainly barytes with pockets of witherite, runs east-west through Wenlock shales and has been worked for a length of 500 m. Witherite also occurs on dumps of several disused mines near Llanidloes, Montgomeryshire, near the foot of a reservoir dam. Some 250 tonnes were produced from this area between 1874 and 1884. Witherite associated with barytes also occurs at Llangynog where lead and zinc were once mined.

Witherite is a rare mineral in *Scotland* where it was discovered in 1918 in Dumfriesshire in the New Glencrieff vein near Wanlockhead as botryoidal masses up to 200 mm in diameter intimately associated with barytes, of which it is considered to be a secondary product due to alteration of barytes.

Barium chloride Barium chloride is widely distributed in brines in the Coal Measures of the Durham and Northumberland Coalfield, and in some mines in the East Midland Coalfield. Brines containing barium chloride were exploited for blanc fixe manufacture at the Eccles Pit, Backworth, Northumberland, in 1970 (see Blanc fixe section of Part III.).

Uses, specification and price

Witherite has been used commercially in case hardening, sugar refining, in the manufacture of heavy clay products to prevent scum, in barium peroxide manufacture, water and brine purification, and in the manufacture of barium chemicals, glass and enamelled iron ware. It is also claimed to be an effective rat poison. The quantities that were used for different purposes, however, are not known. Witherite, when available, was used in preference to barytes as the starting point for the manufacture of barium chemicals.

British Standard Specification BS 1795: 1952 *Extenders for Paints* requires natural witherite to contain not less than 93 per cent of barium carbonate. However it is no longer used for this purpose. No other industrial use specifications are known.

Crushed or ground witherite generally fetched a price nearly double that of the crude ore. The price quoted in 1969 for finely ground witherite was about £30 per tonne for 90 per cent barium carbonate. Witherite always sold at a price higher than barytes but below that of chemically prepared barium carbonate.

Technology

Witherite ore from the Settlingstones Mine was subjected to a gravity concentration process. After preliminary hand picking to remove stone, barytes and large pieces of witherite, the ore was passed through a jaw crusher and thence via an elevator to vibrating screens to produce four fractions, viz: oversize (+ 8mm), (–8mm + 5mm), (–5mm + 3mm), and (–3mm). The oversize passed to a pair of crushing rolls for return to the screens. The two larger fractions were then treated on Harz jigs to produce witherite and gravel. About 70 per cent of the mineral was recovered from the mined ore.

The UK's almost unique production arose from the presence of ore-bodies containing almost pure witherite. The mineral also occurs intimately mixed with baryte, but no process for the physical separation of witherite from baryte is known. Chemical separation, although theoretically feasible, is economically unacceptable.

Production

Northumberland was usually the main British producer of witherite, chiefly from Settlingstones Mine. Total UK witherite production between 1854, when statistical records started, and 1969, when the last operating mine ceased, amounted to 885,000 tonnes.* At the beginning of the 20th century, annual production was about 8,000 tonnes and increased gradually until the Second World War (see Fig 3). A peak production of 20,000 tonnes was reached in the years 1954 and 1955. Output in 1960 was around 10,000 tonnes p.a. In the last financial year of operation of the main producing mine production was about 5,000 tonnes of witherite; it closed at the end of March 1969.

From its first production in 1932 to the closure by the NCB in 1958, the South Moor Colliery (Morrison North Pit, including the old Louisa and Craghead collieries) near Burnhope, north-west Durham, produced between 6,000 tonnes and 16,000 tonnes of high-grade witherite per annum (out of a world production at the same time of between 20,000 and 25,000 tonnes per annum), thus accounting for most of the balance of total UK production.

The decline in UK production was related to rising costs of working, and to the exhaustion of the more readily available ore.

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* See Table 6.

Table 6 United Kingdom: Production of witherite, 1854–1969

Period	*Thousand tonnes*
1854–1860	12
1861–1870	31
1871–1880	42
1881–1890	69
1891–1900	72
1901–1910	76
1911–1920	64
1921–1930	84
1931–1940	93
1941–1950	135
1951–1960	152
1961–1969	55
Total, 1854–1969	885

Sources:
1854–1919: Ministry of Fuel and Power. Report of the Mineral Development Committee (Westwood), Cmd 7732, 1949.
1920–1938: Mines Dept, Annual Report.
1939–1947: Ministry of Fuel and Power.
1948–1969: Department of Trade and Industry records (partly unpublished).

Approximately half a million tonnes of the recorded production was obtained before 1939. Details of this production are given in Table 7.

Table 7 United Kingdom: Details of witherite production, 1854–1938

District	*County*	*Country Rock*	*Production (Tonnes)*
Northern Pennines	Northumberland	Carboniferous Limestone Series	455,065
	Cumberland		5,269*
Durham Coalfield	Durham	Coal Measures	40,690
Shropshire and Wales	Shropshire	Ordovician	956
	Flintshire	Silurian	3,142
	Montgomeryshire		254
Total UK (England and Wales)			505,376

* Including 1,679 tonnes of barytocalcite from Blagill Mine.

Source: Barium Minerals in England and Wales. GS and M Wartime Pamphlet No 46, 1945.

The annual production of witherite in the United Kingdom between 1940 and 1969 is shown in Table 8 below.

Table 8 United Kingdom: Production of witherite, 1940–1969*

Year	*Thousand tonnes*	*Year*	*Thousand tonnes*	*Year*	*Thousand tonnes*
1940	13	1950	17	1960	9
1941	10	1951	18	1961	9
1942	13	1952	18	1962	7
1943	12	1953	15	1963	7
1944	11	1954	20	1964	7
1945	11	1955	20	1965	7
1946	15	1956	17	1966	5
1947	15	1957	18	1967	6
1948	15	1958	8	1968	5
1949	16	1959	9	1969	2

*UK production figures are generally available only to the nearest 1,000 tonnes.

Sources: 1940–1947: Ministry of Fuel and Power, Annual Digest of Statistics.
1948–1970: Department of Trade and Industry records (partly unpublished).

Consumption and trade

Estimated consumption of witherite in the United Kingdom reached a record of 18,000 tonnes in 1955 but fell to 2,000 tonnes in 1969 when the only producer went into liquidation. Exports, mainly to the USA, ranged from about 5,000 tonnes in 1952 and 1953, to about 1,000 in 1960, 1962 and 1967. Exports of witherite are not identified in official United Kingdom statistics, but are distinguished in US and Australian import statistics. According to figures provided by operators, 205,000 tonnes of witherite were retained and used in Great Britain between 1948 and 1970. United States import statistics are shown in Table 9.

Table 9 Imports of witherite from the United Kingdom into the United States, 1948–1969

Year	*Quantity tonnes*	*Fob value £ sterling*
1948	2,241	33,900
1949	1,917	22,600
1950	1,895	18,300
1951	1,829	18,500
1952	4,694	65,700
1953	4,471	63,900
1954	4,005	54,700
1955	2,144	27,800
1956	2,662	39,300
1957	2,748	49,500
1958	2,032	38,600
1959	2,315	40,400
1960	1,264	22,300
1961	1,500	24,000
1962	1,358	21,000
1963	2,522	42,700
1964	2,201	35,400
1965	2,354	40,700
1966	2,022	38,500
1967	1,166	20,000
1968	1,864	31,700
1969	416	9,200

Source: IGS compilation and interpretation of US Bureau of the Census data.

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PART III BARIUM CHEMICALS AND DERIVATIVES

Raw materials and industry

Barytes is now virtually the only source of all barium chemicals and their derivatives. There are over a hundred general chemicals containing barium. Formerly, witherite was the preferred raw material for barium chemical manufacture, but it is no longer available. Barium-rich brines are a very minor source of some barium chemicals. For barium chemical manufacture the ore is required to be in lump form, with a low fluoride content. For this reason, material derived by flotation in Derbyshire as a by-product of fluorspar production cannot at present be used, and the UK barium chemical industry is obliged to import about three-quarters of its raw material requirements.

The barium chemical industry in the United Kingdom is largely concentrated at Widnes. Easy import facilities for overseas ore, and more recently a development area grant for factory construction were contributory factors in the selection of Widnes. The Laporte barium chemical works at Luton was closed in 1966 when production was transferred to Widnes.

The main producer of barium chemicals is Barium Chemicals Ltd of Widnes, now owned on a 50:50 basis by Laporte Industries Ltd and RTZ (Britain) Ltd, which was formed in 1964 by Laporte Chemicals Ltd and Imperial Smelting Corporation Ltd pooling their barium chemical manufacturing activities. McKechnie Chemicals Ltd, also of Widnes, produced lithopone until 1969, but have now abandoned all barium chemical production.

Barium metal

The metal has a white, metallic lustre, but it is yellowish white when it contains nitrogen. It is volatile *in vacuo,* and can thus easily be sublimed. It melts at 710°C and boils at 1500°C. As it is highly reactive, and as it is the least volatile of the alkaline earth metals, it is recommended as a 'getter' for removing gas traces from vacuum tubes. Barium is used as a deoxident in the production of high purity metals such as copper. In the presence of oxygen it burns readily to the oxide when heated. The metal is prepared by the Guntz process by heating barium oxide and peroxide in an electric furnace at about 1200°C *in vacuo* with a metal having a high heat of oxidation, eg aluminium. Metallic barium is available in commercial quantities, but on account of its oxidisable character it must be protected from the air. It is supplied packed in argon-filled plastic bags, inside argon-filled steel containers.

Barium alloys

Some barium alloys are pyrophoric, others are non-pyrophoric. A range of barium-aluminium and barium-magnesium alloys, containing 25 to 50 per cent of barium have been prepared for use as 'getters' and are known as 'Baral' and 'Barmag' respectively. Various lead-based bearing alloys have been developed containing small quantities of barium, eg 'Frary metal' which contains about 2 per cent of barium. Some barium-nickel alloys have been used in sparking plugs. The use of barium alloys in electron emission elements in electronic tubes is due to the high electron emission of barium when subjected to electrical potential. Some barium alloys have been made by fusion electrolysis using a heavy metal cathode in which the heavy metal may be also as a salt, or taken from a subsidiary soluble anode.

Barium compounds

A small number of barium chemicals are manufactured and consumed in the UK in quantities of a thousand tonnes or more a year. They also form the starting points from which a wide range of about 70 compounds are prepared, some of which are used yearly on a scale of hundreds of tonnes, but others only a few tonnes. The barium chemicals now manufactured in the UK include barium carbonate, barium hydroxide, barium sulphate and barium sulphide. Barium oxide, barium nitrate and lithopone were formerly manufactured in the UK but, as far as is known, present reduced requirements are now essentially met by imports.

Soluble barium salts are highly toxic by ingestion by human beings, but the only toxic effect from the industrial point of view is the benign respiratory condition known as baritosis. Barium salts require special labelling for transport.

Barium azide, BaN_6, forms monoclinic crystals which explode when shocked or exposed to heat. Industrially it is applied as a saturated solution to electronic valve components. It quickly decomposes when heated *in vacuo,* liberating nitrogen and leaving barium metal which acts as a 'getter'.

Barium carbonate, $BaCO_3$, occurs naturally as witherite. The chemically prepared substance is scheduled as a poison, but witherite unless finely ground is not. Barium carbonate is the raw material from which most barium compounds are produced. Many thousands of tonnes are manufactured at Widnes each year, and several hundred tonnes are imported. It is generally prepared from the sulphide solution by double decomposition and precipitation, using sodium carbonate, producing sodium sulphide as a valuable by-product. Barium carbonate can also be prepared by dissolving barytes in fused sodium chloride and adding sodium carbonate to the melt. Although this process is claimed to yield a product free from objectionable sulphur compounds, it is not used commercially in the United Kingdom. Barium carbonate is available in several grades of granularity and purity, according to the uses for which it is intended. Thousands of tonnes of ore are consumed annually in the production of special glass for television sets, the barium acting as a barrier to X-rays.

For colour television tubes in the USA strontium carbonate may replace barium carbonate, but British manufacturers appear to be well satisfied with the protection provided by barium glass.

The optical glass industry is also an important, but smaller, consumer of barium carbonate. Barium glass has a higher refractive index, greater brilliancy, elasticity and toughness than lime glass. A mixture containing barium carbonate, sulphate and sulphide has been used in the manufacture of pressed and blown glass. The mixture increases the fluidity of the glass, permitting the moulding of sharp corners and intricate patterns.

Ceramic grade barium carbonate is used in the brick industry to prevent efflorescence. It precipitates sulphates as barium sulphate, and calcium and magnesium as the carbonates. With the closure of the Settlingstones witherite mine, this demand for precipitated barium carbonate has increased. The addition of about 9 kg of barium carbonate per 1,000 bricks eliminates the scum which tends to form on the surface of the brick on drying, resulting in bricks with better colour and diminished porosity. It is rarely used as a flux in pottery because, although it may increase translucency and fired strength, it causes excessive shrinkage and blistering. It is, however, frequently included in enamel compositions in quantities of up to 10 per cent for its properties as a flux. It reduces the fusion temperature otherwise required for high silica enamels and also improves acid resistance.

In the preparation of welding rod coatings, barium carbonate is added as a fluxing ingredient.

Finely divided charcoal intimately mixed with barium carbonate forms carburising compounds. These are applied to the surfaces of iron and steel castings which are heated to 800 to 900°C and quenched in cold water to produce a hard-wearing, high-carbon surface or skin on the metal surface. Barium carbonate is added to heavy drilling muds intended for drilling through gypsum as it helps to prevent the build-up of anhydrite on the drilling bit.

Barium carbonate is also used in the synthetic fibre industry as a desulphonating agent. It is added to plating solutions containing chromium to precipitate insoluble barium chromate and remove a serious public health hazard.

Barium carbonate is commonly used in the USA and Australasia for softening industrial water supplies and boiler feed water. Water softened by this process is, however, unsuitable for drinking or food preparation. It has been used as a rodent poison, for example, dusted on oil palms to prevent damage from rats to the plant and foliage.

An outbreak of gastroenteritis has been reported due to barium carbonate intended for rat poisoning being placed in error in flour used to make pastry. Muscular paralysis has also been reported as a result of the accidental substitution of barium carbonate for flour in sausages.

Barium carbonate is the starting point for the manufacture of barium ferrite and barium titanate.

In January 1972 the quoted price was £66 per tonne.

Barium chloride is available both as a colourless water-soluble crystalline material $BaCl_2.2H_2O$) and in the anhydrous form. It is prepared for use within the company by Barium Chemicals Ltd, and was formerly made from barytes by McKechnie Chemicals Ltd at Widnes up to 1969. Over 4,400 tonnes of barium chloride, worth nearly £200,000 were imported in 1970, mainly from France. Two high purity grades are manufactured in the UK by Johnson Matthey Chemicals Ltd. Barium chloride is usually made via the sulphide by adding calcium chloride to the aqueous solution and evaporating to crystallization. Barium chloride was formerly produced in the UK from witherite, but the National Coal Board, who owned the plant, closed it down in 1956 because of raw material difficulties. It also occurs in brines found in the Coal Measures of the Durham and Northumberland coalfields and in some mines in the East Midland coalfield. These brines have been exploited for blanc fixe preparation. Barium chloride is used for heat treatment baths for steel, either alone, or mixed with potassium chloride. The molten material is free from fuming and can be held at practically any temperature within the range needed for tempering steels.

Barium chloride is reported to be a constitutent of a ternary eutectic salt used as a fire extinguisher for uranium or plutonium fires but there is a toxic hazard associated with its use.

Barium chloride is used as a mordant for fixing acid dyes, in the leather and textile industries. It is the raw material for the preparation of metallic magnesium. It is a very useful laboratory reagent.

The January 1972 quoted price was about £52 per tonne.

Barium chromate, $BaCrO_4$, is precipitated as a yellow crystalline powder when potassium chromate or bichromate is added to a solution of a barium salt. It is used as a pigment in water-colour paints under the name of 'lemon yellow' or 'yellow ultramarine', 'baryta yellow', 'steinbuhl yellow' or 'gelbin'.

Barium ferrite, $BaFe_{12}O_{19}$, has very large crystal anisotrophy and very high coercive force. It has been manufactured in the United Kingdom for over 15 years by kiln firing a mixture of iron oxide and barium carbonate and is sold under the trade name 'Baslox' in a number of grades. It is stable magnetic material which can withstand strong adverse magnetic fields and varying temperature conditions without permanent loss of magnetisation. It is used as a permanent magnetic material for field magnets in DC motors. These DC motors are used in hair driers, record player turntables, electric clock movements, magnetic filtration of oil, and in windscreen wipers. Formerly, a major use was in focus rings for television tubes, but with the introduction of electrostatically focused picture tubes this market outlet failed. The alternative use in the DC motor field was quickly penetrated and the traditional copper field coils and lamination stacks were replaced by barium ferrite permanent magnets. Barium ferrite magnets are reported to have properties which compare well with those of the more expensive alnico class of permanent magnets; their use reduces requirements for nickel and cobalt for magnetic materials.

Barium fluoride, BaF_2, is used in crystal form in lasers. When doped with uranium it has an output wavelength of 26,000 angstroms. It has also been used in embalming fluids and in enamels for ceramics.

Barium hydride, BaH_2 is formed when barium is heated to about 200°C in hydrogen. It is a grey powder which decomposes on contact with water, and can be used as a source of nascent hydrogen for life rafts.

Barium hydroxide, $Ba(OH)_2$, known also as barium hydrate, caustic baryta, and baria hydride, is prepared commercially at Widnes from barium sulphide by double decomposition techniques. It is strongly alkaline, absorbs carbon dioxide from the atmosphere, especially under moist conditions, and is readily soluble in water. It is used for many purposes in the chemical, oil and plastics industries. In conjunction with caustic potash it is used in the preparation of electrolyte for alkaline type electric storage batteries. It is also used in lead acid storage batteries for depositing sulphate on the negative plates. Barium hydroxide is used for saccharate extraction from molasses in sugar refining. It may also be used in place of barium carbonate to fix soluble sulphates in clays used in the manufacture of tiles, sanitary ware and domestic pottery. It is a convenient starting point for the manufacture of barium acetate, oleate, stearate, ricinoleate, napthenate and laurate, and it is used in glycerine refining and in grease manufacture. In connection with methods of smoke reduction from diesel fuels, additives based on barium hydroxide have been used. It can be used in the preparation of inorganic gelling agents such as barium zeolite. It is used in the recovery of lanolin from wool greases, and has anti-sludging applications in both the fuel oil and the lubricating oil industries. It is used as a fungicide and mould inhibitor in felts used in the paper industry.

It is also widely used in the preparation of stabilisers for vinyl resins, to inhibit the breakdown of PVC compounds due to heat and light during processing and life.

Barium manganate, BaMnO, is formed as an emerald-green powder when barium carbonate or nitrate are heated with manganese dioxide. It is used as a pigment under the name 'manganese green' or 'cassel green'.

Barium nitrate, $Ba(NO_3)_2$, occurs naturally in Chile as colourless octahedra, soluble in water, to which the name nitrobarite was given. It can be prepared by dissolving witherite or barium sulphide in dilute nitric acid. The commercial grade is no longer manufactured in the United Kingdom, all requirements being imported, mainly from East Germany, for use in pyrotechnics for the production of green flares and signal lights.

The price of barium nitrate in January 1972 was quoted at about £84 per tonne.

Barium oxide, BaO, known also as calcined baryta, is formed when the metal burns in air, but is more conveniently produced by heating the nitrate or carbonate. It is strongly alkaline, caustic and poisonous. Anhydrous barium oxide, prepared from the carbonate, has been used as a desiccating agent.

Barium peroxide, BaO_2, was formerly produced in the UK from 1916 onwards by B Laporte Ltd for use in hydrogen peroxide manufacture. The process was replaced by a new technique a little over twenty years ago, and the demand for barium peroxide is now very limited.

Barium silicofluoride is used industrially as an insecticide.

Barium stearate is used for waterproofing purposes, and in packing for pumps for alkalis.

Barium sulphate, $BaSO_4$, occurs naturally as barytes, form which two types of chemically prepared barium sulphate are manufactured, *blanc fixe* and *barium sulphate BP.* Chemically precipitated barium sulphate, known commercially as *blanc fixe* (and sometimes as baryta) should not be confused with the natural mineral barytes, although some of the uses are somewhat similar. It is manufactured at Widnes by treating barium chloride with sulphuric acid. Blanc fixe may also be made by adding sodium sulphate to barium chloride solution, including natural brines which have been exploited by the National Coal Board for some years at the Eccles Pit near Shiremoor, Northumberland. The blanc fixe produced was sold to the paper industry. Nearly 6,000 tonnes of blanc fixe, worth over £244,000 was imported in 1970.

Blanc fixe is a neutral, almost completely inert, white powder which is opaque to X-rays, chemically stable to both heat and light, and low in water-soluble, oxidisable and other reactive impurities. It is used as an extender for high opacity white pigments. It is produced in two grades, standard and fine particle, the latter quality being of special interest to the printing ink industry. Barium sulphate is used in 'fining' glass. During the melting there is a considerable evolution of gas, which leaves up to 10 per cent of dissolved gases and bubbles in the molten glass. The removal of this gas is known as fining. If this gas is not removed, the small bubbles blemish the product, and further bubbles are produced when the glass is reheated. Barium sulphate melts only in the hottest part of the furnace, forming large gas bubbles which sweep out and collect small bubbles on their way to the surface. It is reported to be superior to sodium sulphate for 'fining' as it decomposes at a higher temperature and sinks in the glass, whereas sodium sulphate tends to float on the surface.

Blanc fixe is used as a filler and as an ingredient for coating glazed papers and photographic paper. Photo-grade blanc fixe has a particle size of about half a micron. Because of its limited opacity blanc fixe is easier to tint than other pigments. It is readily adapted to the tint correction usually applied on the blue side to overcome the yellow tint of the emulsion gelatine. Its extreme insolubility prevents any interaction between the pigment coat and the sensitive silver halide photographic emulsion. Blanc fixe is readily dispersible in gelatine. It is included in plasters for X-ray rooms, and is a convenient material for filling the insterstices between pieces of aggregate used in X-ray shielding.

The price of standard blanc fixe in January 1972 was quoted as £59 per tonne, and Fine Particle Grade, £82 per tonne.

Barium sulphate BP is an exceptionally pure form, with a very fine and consistent particle size, which makes it readily dispersible. In order to meet the standard of the British Pharmacopoeia it is required to have a very high degree of suspensibility. Because of its opacity to X-rays, it has long been recognised as the ideal substance for the X-ray examination of the alimentary tract. In addition to domestic production, nearly 25 tonnes of barium sulphate BP were imported in 1970 at a cost of over £3,700.

Barium mono-sulphide, BaS, has traditionally been the first intermediate compound formed in the production of all barium compounds and lithopone from barytes. It is a Schedule 1 poison, being strongly alkaline, and contact with the eyes, skin or hair should be avoided. It is prepared in very large quantities in Widnes by heating crushed lump barytes with coke in a kiln fired to about 1,100°C to 1,300°C. The product, commonly called 'black ash', is leached with water and an impure solution of barium sulphide is obtained. The solution may be evaporated to yield a crude technical grade product in the form of brownish-black lumps that contain 60 to 70 per cent BaS. In the UK barium sulphide is supplied as a dark grey powder containing approximately 70 per cent water soluble barium sulphide, the balance being chiefly water insoluble barium compounds and unreacted carbon. In conjunction with cadmium and other metal salts, it is used in the production of colours, mainly yellows and reds. It is also used in the plating industry to provide special metal finishes and in an electrolytic process for the recovery of copper from residues left in the slag produced in platinum refining. Some barium sulphide is used in the preparation of luminous paints.

The price of barium sulphide in January 1972 was quoted as £60 per tonne.

Barium sulphocyanide, also known as barium rhodanide, has been used in the manufacture of sulphocyanides, in dyeing textiles, and in photography.

Barium titanate, $BaTiO_3$, an important synthetic mineral, is used both as single crystals, and in polycrystalline form in ceramic bodies. It exists in several modifications: below -70°C it is trigonal and ferroelectric; from -70°C to +50°C it is orthorhombic and ferroelectric; from +50°C to +120°C it is tetragonal and ferroelectric; above 120°C it is cubic and non-ferroelectric. The strength of the piezo-electric effect makes it very useful, in crystal form, in transducers for sounding, ie finding the depths of oceans for navigation and safety. It is used in sonar to generate sound waves for underwater applications, and as a pick-up in various types of instruments used to measure vibrations. It is used in ultrasonic crack detectors. The piezo-electric properties are utilized in geophones used in seismic prospecting.

Barium titanate shows characteristics not found in other materials in the ceramic field and has important applications for the electronics industry. The ceramic body is prepared, basically, by mixing equimolecular proportions of barium carbonate and titanium dioxide and heating to 135°C. The calcined mass is ground very finely, mixed with a binder, formed into the required shape and manufactured by single state sintering techniques to avoid the presence of glass which would raise the loss factor. Because of its high dielectric properties it is used in miniature condensers for the electronics industry.

Lithopone, a mixture of barium sulphate and zinc sulphide, is precipitated by the interaction of solutions of barium sulphide and zinc sulphate. The precipitate is washed free from zinc sulphate, filter pressed, dried at 50° to 60°C, calcined at a dull red heat, quenched in cold water, wet ground and dried. As first made in 1869 by T and W Griffiths it tended to discolour rapidly. An improved type, first manufactured in Glasgow in 1872 by J B Orr, was known for many years as 'Orr's white'. Production began some years later at Widnes, and continued there until 1969. To produce really good lithopone the solutions used should not contain any appreciable quantities of lead, copper or manganese as these impurities can cause a rapid greying of the pigment in paint. Small quantities of other metals can also have adverse effects on the light fastness, whereas certain others have been used as additives to produce improved qualities. About one tonne of barytes is consumed to produce one tonne of lithopone. Lithopone was used on a large scale in paints for many years. When used for outside paintwork, lithopone tends to weather and to show chalking. On ironwork there is a tendency for free sulphuric acid to be generated by oxidation of the zinc sulphide, causing corrosion. Unlike white lead, lithopone is non-poisonous and is not affected by sulphurous gases. Lithopone is marketed according to its content of zinc sulphide, generally about 30 per cent, but sometimes up to 60 per cent.

Some years ago about 75 per cent of all lithopone consumed went into paints, varnishes and lacquers; coated fabrics and textiles used about 8 per cent; floor coverings 5 per cent; rubber manufacture 3 per cent and paper production about 2 per cent. The lithopone consumption by the paint trade has decreased very considerably in recent years, having largely been replaced by titanium dioxide, which has a better opacity and is free from corrosion risks on outside ironwork. Although lithopone is now little used in paint, the standard grade continues to be the main pigment in oil-bound distempers. Both standard and 60 per cent grades of lithopone are used in some modern types of emulsion paints for interior use.

There has been no production in the United Kingdom since 1969 when McKechnie Chemicals Ltd closed down their lithopone plant at Widnes. For many years it has been imported into the United Kingdom in substantial quantities from Germany. In 1930 and 1931 these imports appear to have been of the order of about 20,000 tonnes, but in 1950 the quantity was about 12,000 tonnes, rising to around 14,000 tonnes in 1951 and falling to under 3,000 tonnes in 1960. In 1970, UK lithopone requirements were met exclusively by imports mainly from West Germany, total imports being nearly 5,000 tonnes valued at over £260,000. There was at one time an export trade in lithopone, UK exports in 1960 and 1961 being over 6,000 tonnes.

The price of lithopone containing 30 per cent of zinc sulphide was quoted at £68 to £70.50 per tonne delivered in January 1972.

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