Molybdenum

Front cover photo: European Court of Human Rights, Strasbourg, clad with 5000 m^2 of S31600 stainless steel, containing 2-3% Mo.
Background: Mo Pins for Sinter Glass Diodes

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MO...MOLY...MOLYBDENUM:

Molybdenum is a metallic element which is most frequently used as an alloying addition in alloy and stainless steels. Its alloying versatility is unmatched because its addition enhances strength, hardenability, weldability, toughness, elevated temperature strength and corrosion resistance.

Although molybdenum is primarily used in steels, its complex and unique properties have proved invaluable in a constantly expanding range of other alloy systems and chemicals.

One of the unique features of molybdenum, as distinct from other heavy metals, is that laboratory tests have shown its compounds to be of low toxicity.

PERIODIC TABLE

V	Cr	Mn
Nb	42 Mo	Tc
Ta	W	Re

PROPERTIES

Atomic Weight:	**95.95 g/g atom**
Density:	**10.22 g/cc**
High Melting Temperature	**2610°C**
Lowest Thermal Expansion Coefficient of the Engineering Metals:	**4.3×10^{-6}/°C**
High Thermal Conductivity:	**142 W/m•K at 20°C**
Crystal Structure: Body-Centred Cubic; Lattice Constant:	**a=3.1468 Å**

PRIMARY CONSUMPTION SECTORS BY END-USE*

Stainless Steels & Super Alloys	**30%**
Low Alloy Steels	**30%**
Chemicals & Mo Metal	**20%**
Tool & High Speed Steels	**10%**
Foundry	**10%**
* IMOA estimates	

Molybdenum was not discovered until the latter part of the 18th century, and does not occur in the metallic form in nature. Despite this, its predominant mineral - molybdenite - was surely utilised in ancient times but would have been indistinguishable from other similar materials such as lead, galena and graphite. Collectively, these substances were known by the Greek word “molybdos”, which means lead-like.

A 14th century Japanese sword has been found to contain molybdenum. However, it was not until 1778 that the Swedish scientist, Carl Wilhelm Scheele, was able positively to identify molybdenum. He decomposed molybdenite by heating it in air to yield a white oxide powder. Shortly thereafter, in 1782, Peter Jacob Hjelm reduced the oxide with carbon to obtain a dark metallic powder which he named “molybdenum”.

Molybdenum remained mainly a laboratory curiosity throughout most of the 19th century until the technology for the extraction of commercial quantities became practical. In 1891, the French company Schneider & Co. first used molybdenum as an alloying element in the production of armour plate. It was quickly noted that, with a density of only slightly more than half that of tungsten, molybdenum was an effective replacement for tungsten in numerous steel alloying applications.

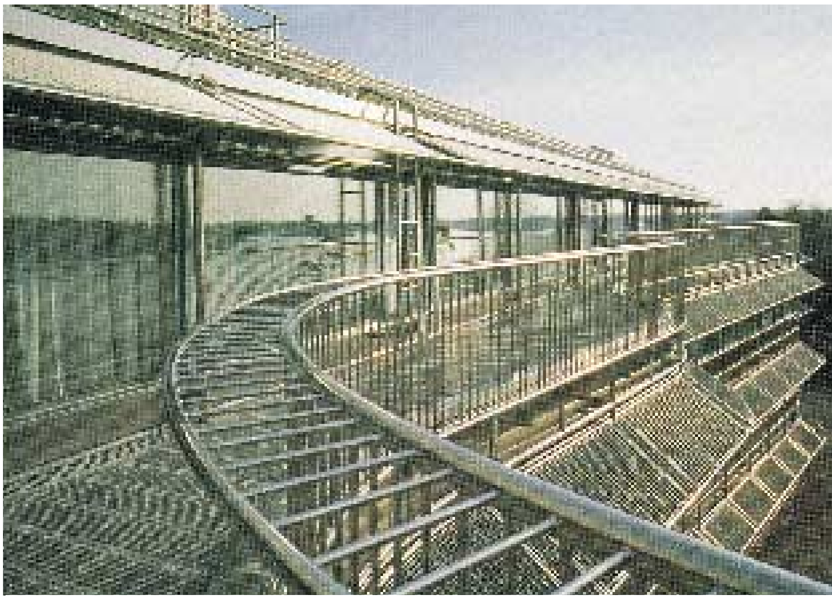
World War I caused tungsten demand to soar and severely strained its supply. As a direct result, molybdenum was substituted for tungsten in many hard and impact resistant steels. The resulting increased demand initiated an intensive search for new sources of molybdenum supply, culminating with the development of the massive Climax deposit in Colorado, USA and its initial operation in 1918.

Whilst the word “molybdenum” was only introduced into the English language around 1816, an analysis of parts of the sword of the famous 14th century Japanese artist, Masamune, proved that it contained molybdenum. *(ref. Sutulov A., Int. Molybdenum Encyclopedia, Intermet Publ., Chile 1978)*

Wills Saint Claire - First automobile constructed with Mo steels

ATOMIC WEIGHT OF MOLYBDENUM: 95.95 g/g atom
ATOMIC WEIGHT OF TUNGSTEN: 183.85 g/g atom

The end of the war and the consequent reductions in demand triggered research efforts to develop new civilian applications for molybdenum. A number of new low-alloy molybdenum automotive steels were soon tested and accepted. The big breakthrough, however, occurred in the 1930's with the determination of proper temperature ranges for the forging and heat treatment of molybdenum-bearing high-speed steels. From this beginning, research eventually developed a full understanding of how molybdenum imparts its many cost-effective benefits as an alloying element to steels and other systems.



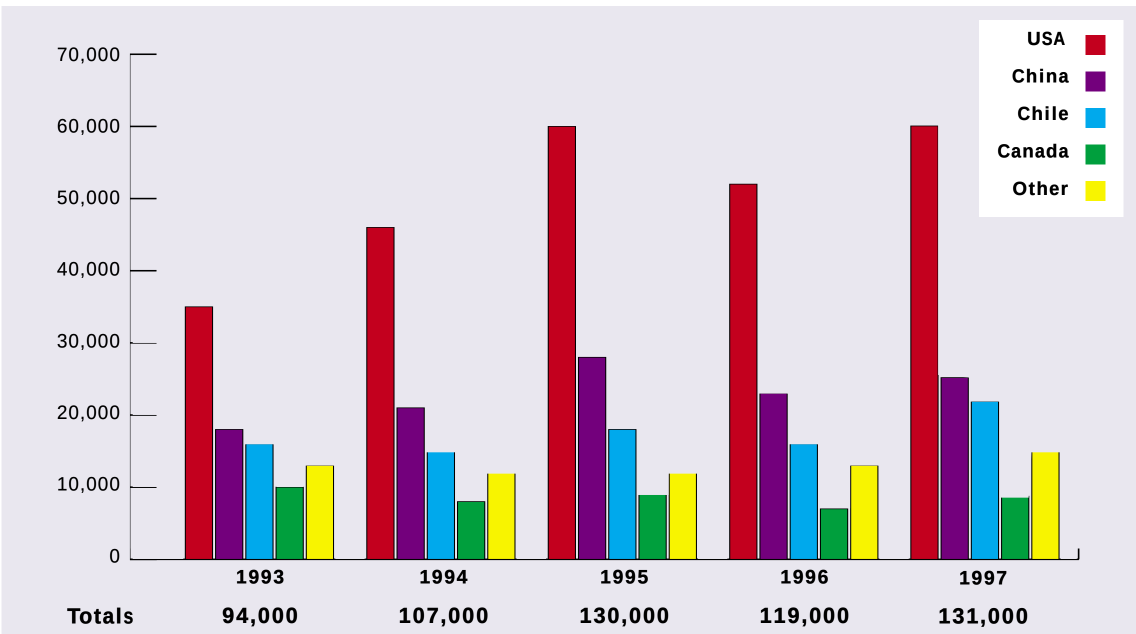
Architectural application of S31600 stainless steel, (2-3% Mo), Finland

By the end of the 1930's, molybdenum was a widely accepted technical material. The conclusion of World War II in 1945 once again brought increased research investment to develop new civilian applications, and the post-war reconstruction of the world provided additional markets for structural steels, many of which already contained some molybdenum.

The years from 1945 to the present have seen a dramatically expanding range of applications for molybdenum, its alloys and its compounds. Rising demand has been comfortably balanced by new sources of assured supply and by new processing technologies with superior recovery rates.

Although steels and cast iron comprise the single biggest market segment, molybdenum's diversity has also proven invaluable in superalloys, nickel base alloys, lubricants, chemicals, electronics and many other applications.

Mine Production*(MT of Mo contained)



Other Countries: Mexico, Peru, Iran, CIS, Mongolia.
'Other' may be understated as estimates for production in the CIS vary.
Mine production is supplemented by recycled material, mainly from spent catalysts

*IMOA Estimate

Molybdenite particles coat bubbles during flotation process

RESERVES

Molybdenum is only known to occur in a natural state chemically combined with other elements. Although a number of molybdenum-bearing minerals have been identified, the only one of commercial significance is molybdenite (MoS_2) - a natural molybdenum sulphide. In ore bodies, molybdenite is generally present in grades from 0.01- 0.50% and is often associated with the sulphide minerals of other metals, notably copper.

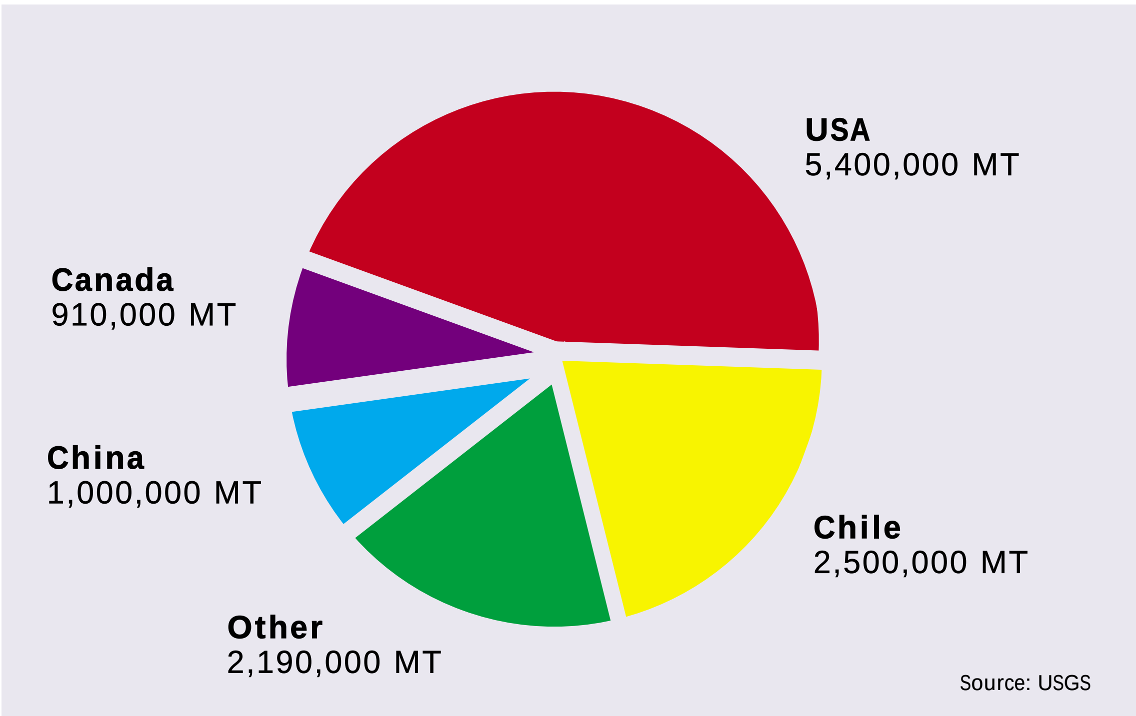
Reserves are mainly located in the western mountain regions of North and South America. The USA is by far the largest producing country, and also has the largest reserve base of 5.4 million tonnes, nearly half of the world's total.

MINES

Ore bodies and mines can be classified into three types:

- Primary mines, where the recovery of molybdenite is the sole objective;
- By-product mines, which remove molybdenite during copper recovery;
- Co-product mines, where commercial viability is dependent upon the extraction of both molybdenite and copper-bearing minerals.

World Molybdenum Reserves (12,000,000 MT)



MINING

The relatively low grade of most Mo ores necessitates the use of high volume low cost mining extraction techniques, most commonly:

- Massive open cast pits; or
- Underground block caving, wherein large blocks of ore are undercut and allowed to collapse under their own weight.

Many molybdenum mines are amongst the most productive in the world, with the largest capable of moving over 50,000 tonnes of ore per day.

MILLING

Mined ore is pulverized through a series of crushers and rotating ball and/or rod mills to fine particles that may be only microns (1/1000th mm) in diameter. This liberates the molybdenite from its host rock. A water slurry of the ore is then conditioned with reagents - including some fuel or diesel oil - which coats the molybdenite particles, rendering them water-repellant.

Separation by flotation takes place in aerated tanks. Molybdenite particles attach to rising air bubbles and concentrate in the surface froth which is swept into overflow troughs. Subsequent regrinding and reflotation stages increase the molybdenite content of the new concentrate stream, by steadily removing unwanted material. The final concentrate contains between 70-90% molybdenite. If required, an acidic leach may be employed to dissolve impurities such as copper and lead.

ROASTING

The roasting process converts molybdenite concentrate into technical molybdenum oxide by the following chemical reactions:

Bingham Canyon molybdenum by-product mine

$$2MoS_2 + 7O_2 = > 2MoO_3 + 4SO_2$$
$$MoS_2 + 6MoO_3 = > 7MoO_2 + 2SO_2$$
$$2MoO_2 + O_2 = > 2MoO_3$$

These take place at 600-700°C in large multihearth furnaces or "roasters". Sulphide concentrate is rabbled from the centre to the periphery of one hearth where it drops to the hearth below and is rabbled back to the centre. It reacts continuously with a steady supply of forced air during the 10 hours it takes to complete the circuit across a dozen or more hearths. The resulting technical grade molybdenum oxide typically contains a minimum of 57% molybdenum, and less than 0.1% sulphur. Desulphurisation systems remove sulphur dioxide from the effluent roaster gases.

Some of the by-product molybdenite concentrates from copper mines contain small quantities (<0.10%) of rhenium, a metallic element used in catalysts for the production of unleaded gasoline and in advanced superalloys for turbine blades of the latest jet engines. Molybdenum roasters equipped to recover rhenium are one of the principal commercial sources for this rare metal.

TECHNICAL OXIDE

Roasted molybdenite concentrates (generally known as "tech-oxide") is the principal product for adding molybdenum to alloy and stainless steels. In order to accommodate individual steel-making requirements, tech-oxide is available in a variety of forms and packaging, eg

Powder: packaged in bulk-bags, drums or cans.

Briquettes: carbon-free "pillow" shaped, and packed in bulk-bags or drums.

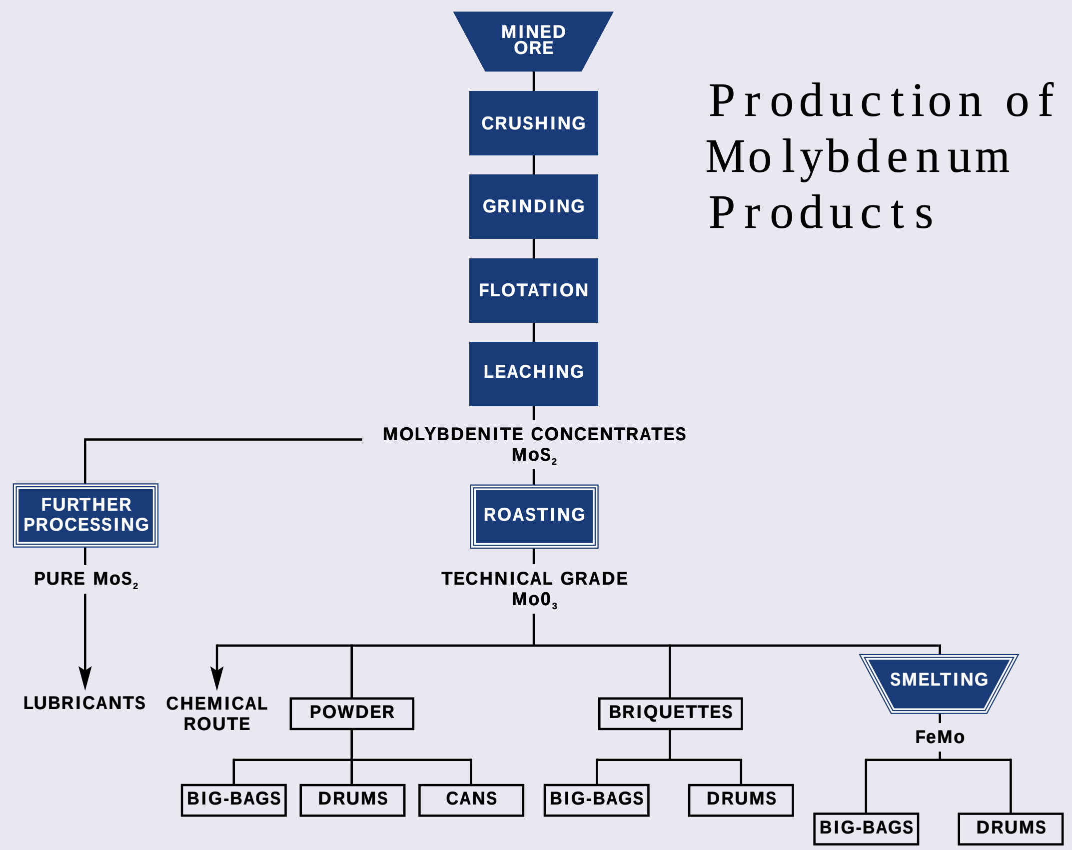
Briquettes: carbon-bonded "pillow" shaped, and packaging e.g.: in 10 kg. boxes.

FERROMOLYBDENUM

Ferromolybdenum (FeMo) is produced by the thermite reduction of tech-oxide in the presence of iron. With a typical analysis of 60-70% Mo (remainder iron), it is used as a molybdenum addition in the ladle or in melting processes, such as induction melting, which cannot reduce the oxide. Higher molybdenum content variations are also available. Western world FeMo production is approximately 45 million lbs Mo annually.

MO METAL

Some molybdenum containing alloys, such as super-alloys, cannot tolerate iron and must be melted with molybdenum metal. This is produced by a hydrogen reduction of pure molybdic oxide or ammonium molybdate. The molybdenum powder is pelletised for ease of handling in the melt shop.



Production of Molybdenum Products

CHEMICAL PRODUCTS

Some technical oxide is further processed into a number of chemical products, and into pure molybdenum metal.

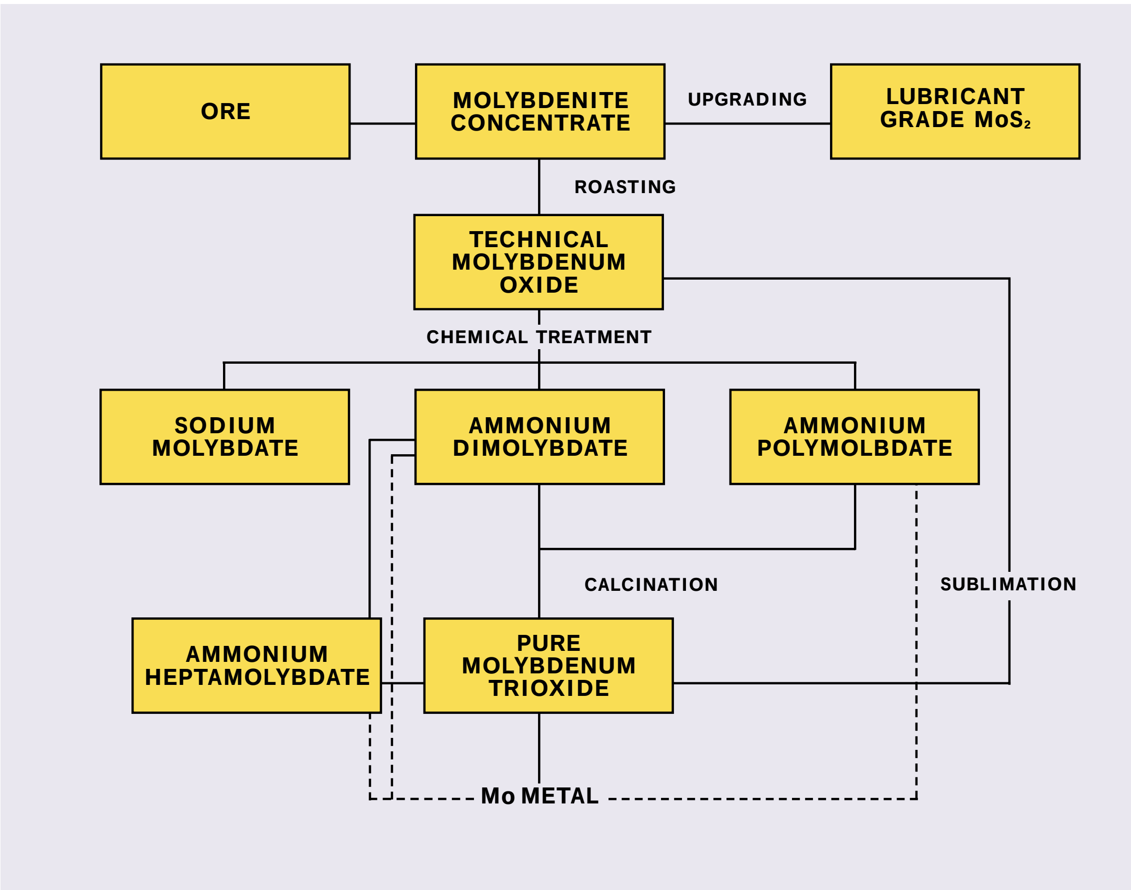
Technical oxide is upgraded by sublimation to produce pure MoO_3, and by wet chemical processes to produce a wider range of pure molybdenum chemicals (mainly oxides and molybdates). The latter involves the initial dissolution in an alkaline medium (ammonium or sodium hydroxide) followed by removal of impurities by precipitation and filtration and/or solvent extraction.

The resulting ammonium molybdate solution is then converted to any one of a number of molybdate products by crystallisation or acid precipitation. These can be further processed by calcination to pure molybdic trioxide.

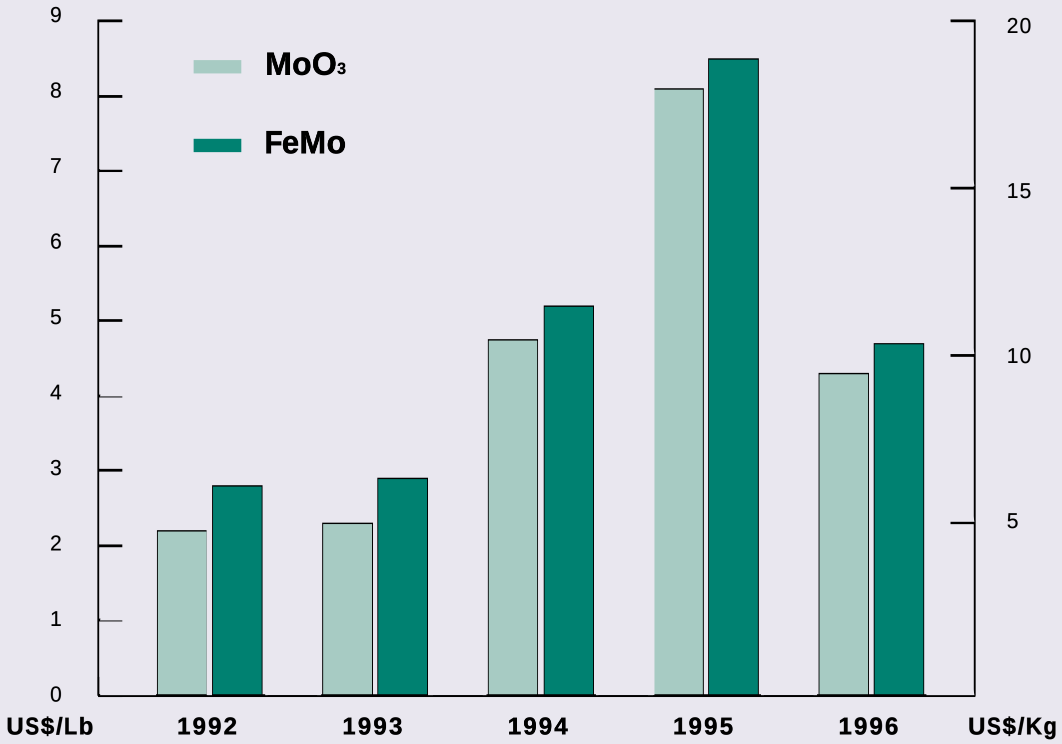
Molybdenum chemicals are extensively applied due to their unique characteristics, such as:

- Catalytic activity in petroleum desulphurising catalysts;
- colourful pigments;
- corrosion inhibitors;
- micronutrients in fertilisers;
- flame and smoke suppression;
- lubricity under extreme pressure and temperature conditions.

Production of molybdenum Chemicals



Annual Average Prices of Technical Grade Molybdenum Oxide in US$/Lb Mo and Ferromolybdenum in US$/Kg Mo



Source: Mo0₃: "Metals Week" Dealer Oxide price FeMo: "Metals Week" European FeMo price

Samples of technical oxide and ferromolybdenum

FERROUS MATERIALS

Molybdenum demand is primarily dependent upon the production of alloy, stainless and tool steels, and cast irons which extensively use molybdenum to:

- minimise the cooling rate necessary to obtain a hard martensite structure and thereby increase strength, hardness, and toughness in large heavy section components;
- reduce temper embrittlement;
- resist hydrogen attack;
- resist sulphide stress cracking (SSC);
- increase elevated temperature strength;
- improve the resistance of stainless steels to a wide variety of corrosive environments, especially chloride pitting resistance;
- improve weldability, especially in high-strength low-alloy (HSLA) steels.

NON-FERROUS ALLOYS

Molybdenum is an important constituent in most superalloys and many nickel and titanium based alloys, wherein: it is a potent solid solution strengthener at elevated temperatures; it increases chloride pitting resistance; it increases corrosion resistance in reducing solutions.

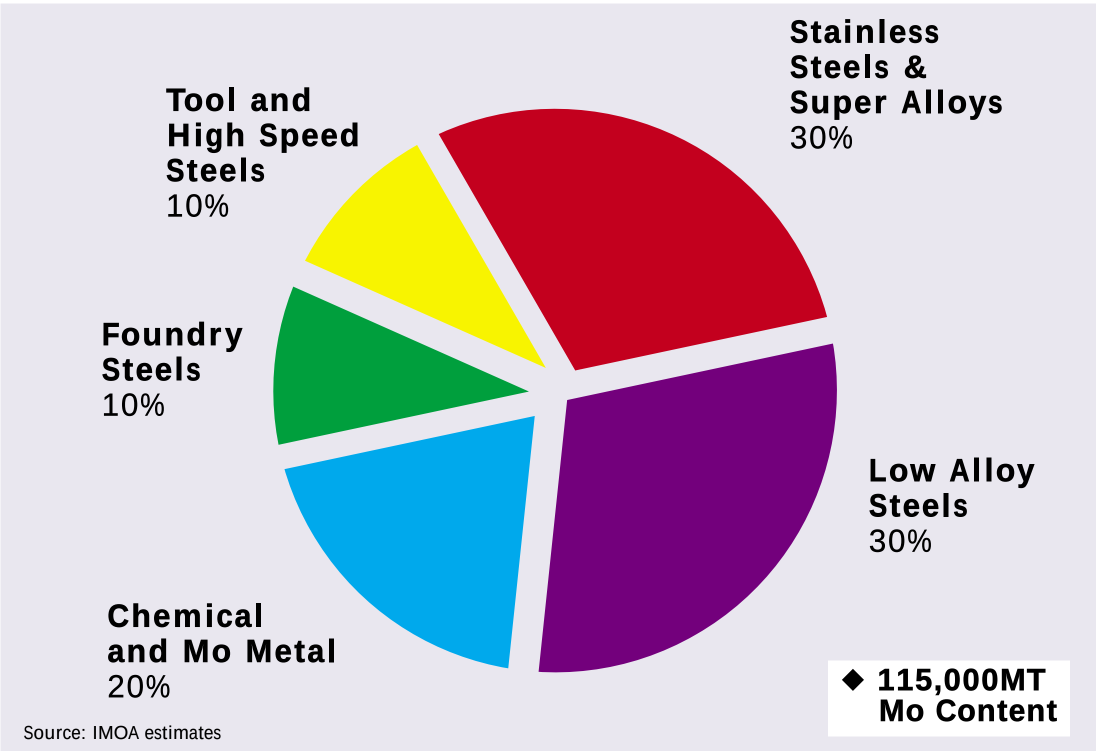
MO BASE ALLOYS

Molybdenum and its alloys are finding ever widening use because of their high strength up to 2000°C, low coefficient of expansion combined with good thermal and electrical conductivity; high resistance to corrosion by molten glass, salts and metals; and good wear resistance in thin coatings.

MOLYBDENUM & STEEL

Molybdenum is an exceptional steel alloying element that not only imparts many unique and useful characteristics to steel but is also easy to add to the molten metal. Melt losses are minimal, whether the molybdenum is added as oxide, FeMo or as Mo-containing steel scrap.

Molybdenum Consumption by End-Use in 1997 (excl. China & CIS)



CARBURISING STEELS

Molybdenum (0.15-0.30%) is used in carburising steels to increase simultaneously the hardenability of the low carbon core and toughen the high carbon case. It is especially effective in large cross sections, such as gears. Molybdenum is not oxidised during carburisation, making it an effective hardening agent which does not cause increased surface cracking and spalling.

Valve casting in Hastelloy CW6M, containing up to 20% Mo to withstand severe corrosion at high temperatures

HIGH TEMPERATURE STEELS

The molybdenum atom is very large relative to other alloying elements. As such, it is a very potent strengthener and increases creep strength up to about 600°C. Its size effectively impedes migration of arsenic atoms to grain boundaries and thereby provides resistance to temper embrittlement. Hydrogen diffusion is also impeded and this minimises hydrogen cracking.

One of the earliest high temperature steels to use these attributes was the carbon-0.50% Mo steel. It has been superseded by a family of Cr-Mo steels which contain from 0.50-2.0% Mo. 2.25 Cr-1.0 Mo steel is a work-horse alloy used worldwide in oil refineries, power plants and petrochemical plants.

HIGH STRENGTH LOW ALLOY (HSLA) STEELS

Molybdenum has played an important role in the development of low carbon, microalloyed HSLA steels. The addition of 0.1-0.3% molybdenum produces a fine grain structure of acicular ferrite and substantially enhances the precipitation hardening effects achieved from other alloying elements.

High yield strengths of 450-600 MPa (65-85 ksi) are achieved in HSLA steels without extensive heat treatment. With a ductile/brittle transition temperature as low as -60°C, these materials have been used in large quantities to build pipelines from remote Arctic oil and gas fields. Thinner gauges of Mo-containing HSLA steels have excellent formability and their high strength/weight ratios make them ideal for the production of automotive structural parts.

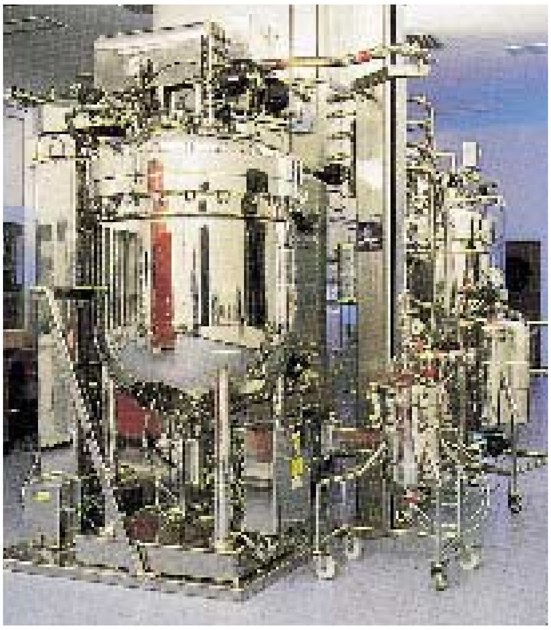
OIL COUNTRY TUBULAR GOODS

The continuous search for new sources of oil has necessitated the exploration and development of very deep reservoirs, often contaminated with corrosive hydrogen disulphide, carbon dioxide and high chloride brines. The AISI 4100 series of Cr-Mo steels, containing 0.15-0.25% Mo, are widely used. A modified AISI 4140 with 0.4-0.6% Mo is the most sulphide stress cracking (SCC) resistant low alloy steel available for use in sour wells. As depths increase and service conditions become more severe, higher molybdenum stainless steels and nickel base alloys, such as alloy C-22 (13% Mo) and alloy C-276 (16% Mo) are increasingly used.

STAINLESS STEELS

Stainless steels are corrosion resistant because the chromium content spontaneously forms a thin, protective passive film on the surface of the steel. Molybdenum enhances this passive film by making it stronger and helping it to re-form quickly if it is disrupted by chlorides. Increasing the molybdenum content increases the pitting and crevice corrosion resistance of stainless steels.

Type 316 (2-3% Mo) is the most widely used Mo-containing stainless steel. It is specified for the tanks, piping and heat exchangers used in food handling and processing and in the production of pharmaceuticals. Increasing the molybdenum content heightens the resistance to wind-borne chlorides and so Type 316 is the material of choice for architectural applications in marine, coastal environments. Type 316 was used

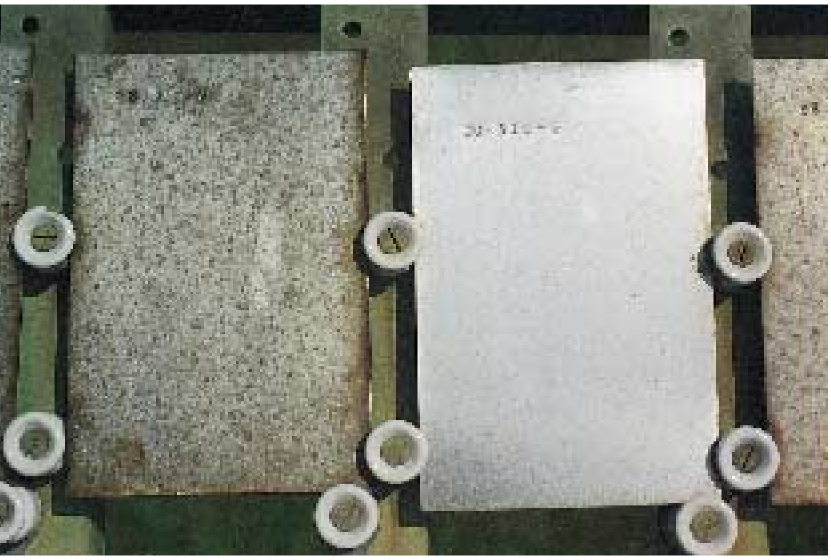


Giusti S31600 stainless steel pharmaceutical manufacturing vessels, (2-3% Mo content)

to clad the exteriors of the Canary Wharf building in London and the tallest building in the world, the Petronas Towers in Kuala Lumpur, Malaysia.

Duplex stainless steels (3-4% Mo) combine high strength and excellent chloride stress corrosion cracking resistance. Initially used for gathering lines in the oil and gas industry, these versatile stainless steels are increasingly being used in the chemical process and petrochemical industries and for digesters in the pulp and paper industry.

The most corrosion resistant stainless steels contain 6 - 7.3% Mo. These grades are used for power plant condensers, offshore piping, and critical components in nuclear power plants such as service water piping. In 1996, 6% Mo stainless steels were selected for the absorber towers of more than twenty flue gas desulphurisation scrubbers being installed in coal-burning power plants in South Korea.



Types 304 (0% Mo) and 316 (2-3% Mo) test panels after 56 years marine exposure

PITTING/ CREVICE CORROSION

The passive chromium oxide layer is most vulnerable near grain boundaries and non-metallic inclusions where minute galvanic cells can form and cause rapid pitting. Oxygen depleted regions, such as those found under gaskets or lap joints, are susceptible to similar attack, but it is usually called crevice corrosion.

Molybdenum is the most potent and cost effective alloying element for preventing pitting and crevice corrosion. Stress corrosion cracking (SCC) can occur whenever applied or residual tensile stresses are present within a stainless steel that is exposed to a corrosive media, especially those containing chlorides and sulphides at elevated temperatures. Higher molybdenum contents are one of the most efficient ways to improve a steel's resistance to SCC.

The illustration above shows Type 304 (0% Mo) and Type 316 (2-3% Mo) test panels exposed for 56 years at the marine atmospheric test facility of LaQue Corrosion Services on the Atlantic Ocean, North Carolina. While Type 316 is not corrosion free, it is in excellent condition after more than half a century in a very severe environment. The stainless steel without Mo is extensively corroded. The photo illustrates dramatically the beneficial effect of molybdenum additions in stainless steels.

The most severe operating environments encountered in power plant scrubbers, pulp and paper and chemical process equipment, require the use of alloys with even higher molybdenum contents. A spectrum of increasingly higher molybdenum alloys includes grades with typically 6 - 8% Mo and nickel base alloys with 10% and 16% Mo.

Sulphuric acid plant for the desulphurisation of flue gases

TOOL & HIGH-SPEED STEELS

One of the earliest applications of molybdenum was as an efficient and cost effective replacement for tungsten in tool and high-speed steels. The atomic weight of molybdenum is roughly half that of tungsten and therefore 1% Mo is roughly equivalent to 2% tungsten. Because these highly alloyed steels are used in the working, cutting and forming of metal components, they must possess high hardness and strength, combined with good toughness, over a broad temperature range.

TOOL STEELS

Molybdenum in tool steels increases their hardness and wear resistance. By reducing the 'critical cooling rate' molybdenum promotes the formation of an optimal martensitic matrix, even in massive and intricate moulds which cannot be cooled rapidly without distortion or cracking. Molybdenum also acts in conjunction with elements like chromium to produce substantial volumes of extremely hard and abrasion resistant carbides.

As the physical demands placed on tool steels increase, so too does the molybdenum content ...

A selection of high-speed cutting tools

HIGH SPEED STEELS

When tool steels contain a combination of more than 7% molybdenum, tungsten and vanadium, and more than 0.6% carbon, they are referred to as high speed steels. This term is descriptive of their ability to cut metals at 'high speeds'. Until the 1950's, T-1 with 18% tungsten was the preferred machining steel, but the development of controlled atmosphere heat treating furnaces made it practical and cost effective to substitute part or all of the tungsten with molybdenum.

	% Mo
Plastic moulding steels	up to 0.5
Cold work steels	0.5 - 1.0
Hot work steels	up to 3.0

Typical Compositions of Selected High-Speed Steels (%)

Grade	C	Cr	Mo	W	V
T-1	0.75	-	-	18.0	1.1
M-2	0.95	4.2	5.0	6.0	2.0
M-7	1.00	3.8	8.7	1.6	2.0
M-42	1.10	3.8	9.5	1.5	1.2

Additions of 5-10% Mo effectively maximise the hardness and toughness of high-speed steels and maintain these properties at the high temperatures generated when cutting metals. Molybdenum provides another advantage: at high temperature, steels soften and become embrittled if the primary carbides of iron and chromium grow rapidly in size. Molybdenum, especially in combination with vanadium, minimises this by causing the carbides to reform as tiny secondary carbides which are more stable at high temperatures.

The largest use of high-speed steels is in the manufacture of various cutting tools: drills, milling cutters, gear cutters, saw blades, etc.

The useful cutting characteristics of high-speed steel have been further extended by applying thin, but extremely hard, titanium carbide coatings which reduce friction and increase wear resistance, thereby increasing cutting speed and tool life.

The exceptional high temperature wear properties of molybdenum-containing high-speed steels are ideal for new applications such as automobile valve inserts and cam-rings.

Mo/Cu and W/Cu Heat Sinks for Thermal Management in Microelectronic Devices

CAST IRONS

Molybdenum increases the strength and hardness of cast irons by depressing the pearlite transformation temperature. It also increases elevated temperature strength and creep resistance. High chromium irons, containing 2-3% molybdenum, exhibit significantly greater impact toughness than Mo-free grade and are ideal for severe abrasive conditions like those encountered in mining, milling, crushing etc. These cast irons have acceptable properties as cast. This eliminates the need for a costly heat treatment and makes them a cost effective alternative to other grinding materials. Reduced levels of austenite formers, such as nickel and manganese, also minimise the retention of low temperature austenite - a potential cause of premature failures.

There has been growing interest in the use of high silicon-molybdenum ductile irons with up to 4% Si and 1% Mo. Their good strength up to 600°C makes them a viable and cost effective replacement for more highly alloyed irons and steels in elevated temperature applications such as turbocharger housings, engine exhaust manifolds and furnace components. The austempered nodular irons develop a unique microstructure capable of strengths in excess of 1000 MPa (145 ksi) with good impact toughness. Their exceptional properties are ideal for critical applications such as the large gears and crankshafts required for power generation, ship propulsion and large mining equipment.

POWDER METALLURGY

The main limitation to increasing the alloy content of highly alloyed, ingot cast materials like high-speed steels is their tendency to segregate during the slow cooling. Powder metallurgical (PM) techniques atomise molten steel into tiny droplets that cool so rapidly that internal segregation is prevented. Steels produced by compaction of these particles have a far more uniform microstructure, which provides numerous advantages over equivalent conventional grades. Many PM high-speed steels, stainless steels and nickel-base alloys are commercially available and, in the future, this technique promises to make possible new generations of highly alloyed steels.

PM techniques enable the superalloy industry to produce more highly alloyed compositions for critical parts, such as gas turbine components.

MO BASE ALLOYS

Molybdenum metal is usually produced by powder metallurgy techniques in which Mo powder is hydrostatically compacted and sintered at about 2100°C. Hot working is done in the 870-1260°C range. Molybdenum forms a volatile oxide when heated in air above about 600°C and therefore high temperature applications are limited to non-oxidising or vacuum environments.

Molybdenum alloys have excellent strength and mechanical stability at high temperatures (up to 1900°C). Their high ductility and toughness provide a greater tolerance for imperfections and brittle fracture than ceramics.

The unique properties of molybdenum alloys are utilised in many applications:

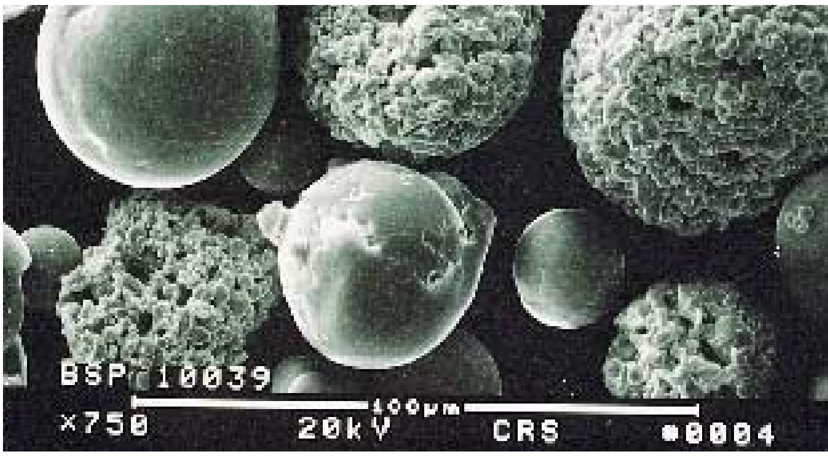
- High temperature heating elements, radiation shields, extrusions, forging dies, etc;
- Rotating X-ray anodes used in clinical diagnostics;
- Glass melting furnace electrodes and components that are resistant to molten glass;
- Heat sinks with thermal expansivity matching silicon for semiconductor chip mounts;
- Sputtered layers, only Ångstroms (10^{-7} mm) thick, for gates and interconnects on integrated circuit chips;

Rotor of a gas turbine, type FR 9001/E, 170 MW, with high Molybdenum-containing steel blades *(Courtesy of Nuovo Pignone, Firenze)*

- Sprayed coatings on automotive piston rings and machine components to reduce friction and improve wear.

For specialised applications, Mo is alloyed with many other metals:

- Mo-tungsten alloys are noted for exceptional resistance to molten zinc;
- Mo is clad with copper to provide low expansion and high conductivity electronic circuit boards;
- Mo-25% rhenium alloys are used for rocket engine components and liquid metal heat exchangers which must be ductile at room temperature.



Spherical Agglomerates of Mo Powder (lacy appearance), with solid spheres of the Ni-Cr alloy binder for the Mo powder

SUPERALLOYS & NICKEL BASE ALLOYS

Molybdenum enhances the corrosion resistance and mechanical properties of nickel base alloys in the same way that it improves the corrosion resistance of stainless steels. Many high molybdenum corrosion resistant nickel base alloys are widely used in applications already mentioned.

Molybdenum is a very potent matrix strengthener in the high temperature superalloys which made jet engines practical. Molybdenum (up to 5%) strengthens the nickel matrix and extends service temperatures by partitioning between the nickel matrix and the gamma prime precipitate phase. These alloys are widely used in the rotating components such as turbine blades and discs of jet engines. Higher Mo alloys, such as alloy X (9% Mo) are used in many stationary combustion components. Today, superalloys comprise over a third of a jet engine's weight. Stellite 21, a 5% molybdenum cobalt base investment casting alloy, has excellent corrosion resistance to body fluids and is widely used in prosthetic devices.

TITANIUM BASE ALLOYS

Additions of up to 5% Mo are used in the alpha-beta type titanium alloys. These materials can be effectively heat treated to strengths in excess of 1000 MPa (145 ksi) and are used in the aircraft industry for jet engine compressor and structural components where low weight, high strength and corrosion resistance are of primary importance.

CHEMICAL APPLICATIONS

Molybdenum-based chemicals have the versatility of chemistry which can occur between the transitions of +4, +5 and +6 oxidation states. Materials made from molybdates are oxidation catalysts, have photo-activity, and can offer semiconducting properties. Many of the properties of molybdenum can provide development opportunities and new commercial applications through the exploration of its chemistry. Compounds of molybdenum can often be made which mimic the chemistry of toxic elements, but which are a safer substitute.

CATALYSTS

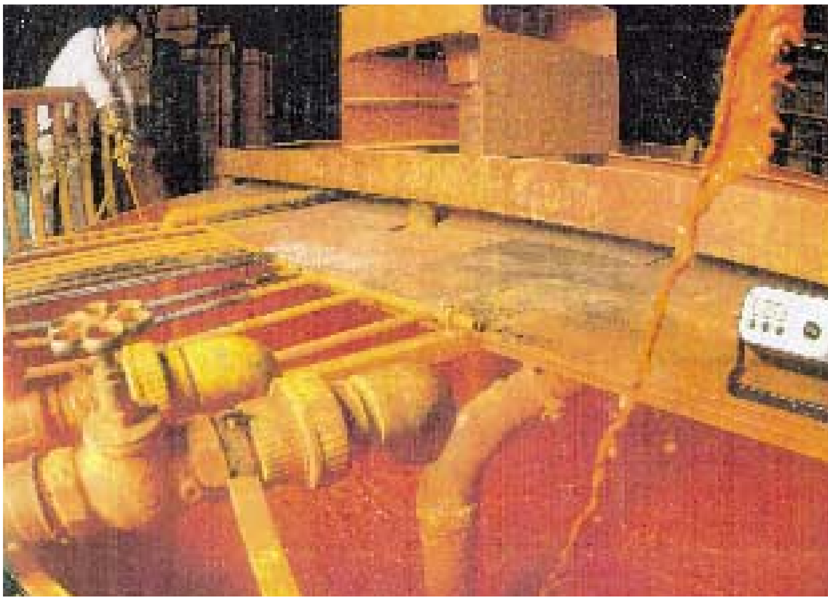
The uses of molybdenum-based catalysts are extensive. When combined with cobalt and nickel, molybdenum is used in the petroleum industry for its ability to remove sulphur from the organic sulphur compounds usually found in crude oil. As the world supply of crude oil is further extended and low-sulphur crudes are less available, molybdenum-based catalysts will increase in use. Mo catalysts can convert hydrogen and carbon monoxide produced by the pyrolysis of waste materials to alcohols in the presence of sulphur, under conditions that would poison precious metal catalysts. Mo has been used in the conversion of coal to hydrocarbon liquids. Molybdenum not only allows for economical fuel refining but also contributes to a safer environment through lower sulphur emissions.

Molybdenum, as a component of a selective oxidation catalyst, will convert propylene, ammonia and air to acrylonitrile, acetonitrile and other chemicals which are important to the plastics and fibre industries.

PIGMENTS

Molybdates are used for two properties, stable colour formation and corrosion inhibition.

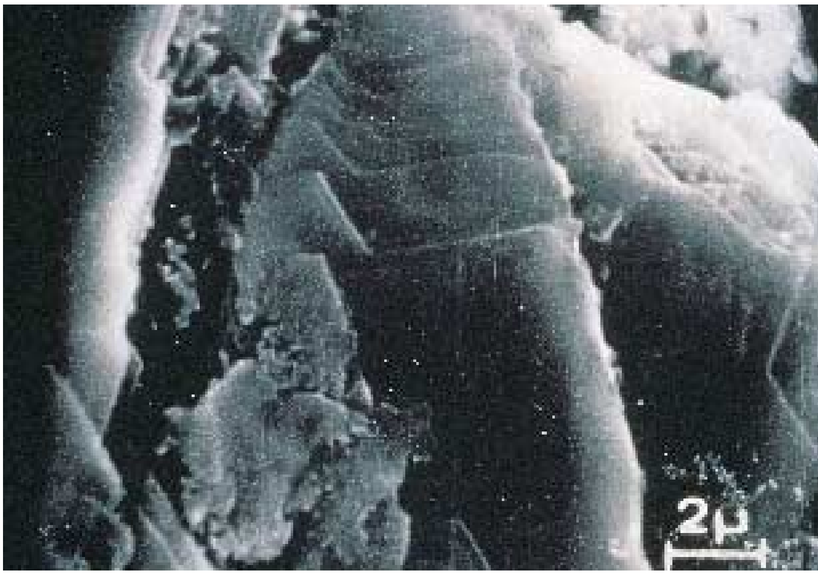
Molybdenum oranges are light and heat stable pigments, from bright red-orange to red-yellow in colour, which are used in paints and inks, plastic and rubber products, and ceramics. Molybdo-phosphoric acid is used to precipitate the dyes Methyl Voilet and Victoria Blue. White corrosion inhibiting pigments are used as paint primers.


Precipitation of molybdenum red pigment

CORROSION INHIBITORS

Sodium molybdate has been used for decades as a substitute for chromates for the inhibition of corrosion in mild steels over a wide range of pH. Molybdates have a very low toxicity and are less aggressive oxidants toward organic additives that are often used in corrosion inhibiting formulations. The protection of mild steel used in the construction of air-conditioning cooling water and heating systems is a prime application. Molybdate solutions protect against rusting of steel parts during machining, and are used in water-based hydraulic systems. It is also used as an additive in automobile engine anti-freeze.

Corrosion inhibiting pigments, primarily zinc molybdate, but also molybdates of calcium and strontium, are used commercially in paints. These pigments are white and can be used as a primer or as a tint with any other colour.



Cross-section of a molybdenum disulphide film showing the plate-like structure

SMOKE SUPPRESSANTS

In electronic technology, wire and cable insulation represents a fire and smoke hazard to firefighters and those in the confines of aircraft and hospitals. Ammonium octamolybdate has been used with PVC to suppress the formation of smoke. These uses and other developments will be increasing as video, telephone and computing networks increase.

LUBRICANTS

Molybdenum disulphide, the most common natural form of molybdenum, is extracted from ore and then purified for direct use in lubricants. This material by itself, since it has a layered structure, makes a very efficient lubricant. These layers can slide over each other at the molecular level, allowing the surfaces of steel and other metals to move fluidly, even under severe pressures, as bearing surfaces. Since molybdenum disulphide is of geothermal origin, it has the durability to withstand heat and pressure. This is particularly true if small amounts of sulphur are available to react with iron and provide a sulphide layer which is compatible with molybdenum sulphide in maintaining the lubricating film. Molybdenum disulphide is inert to many chemicals and will perform under a vacuum where graphite fails.

A number of unique properties distinguish molybdenum disulphide from other solid lubricants:

- A low coefficient of friction (0.03-0.06) which, unlike graphite, is inherent and not a result of absorbed films or gases;
- A strong affinity for metals;
- Film forming structure;
- A yield strength as high as 3450 MPa (500 ksi);
- Stability in the presence of most solvents;
- Effective lubricating properties from cryogenic temperatures to about 350°C in air (1200°C in inert or vacuum conditions).

A combination of molybdate and water soluble sulphides can provide both lubrication and corrosion inhibition in cutting fluids and metal forming materials. Oil soluble molybdenum-sulphur compounds, such as thiophosphates and thiocarbamates, provide engine protection against wear, oxidation and corrosion. Several commercial manufacturers supply these additives to the lubrication industry.

Mo Content	Product Type (%)	Uses
1-20	Greases - for manufacturing, mining and transportation	Ball & roller bearings, splines, chassis. conveyors
20-60	Pastes - mineral or synthetic base	Assembly of machinery, splines, gears, universal joints, metal forming
0.5 - 5	Industrial and Motor Oils or Synthetic Fluids	All automotive and industrial gears, reducers, cams, etc
1-20	Water Suspensions	Metalworking and process lubrication, threads, slides, packings, die casting
Up to 85	Bonded Coatings - air or heat cured, organic, inorganic	Threads, tools, switches, locks, valves, slides, process lubrication, metalworking
1-40	Metalworking compounds Soaps, Powders, etc	Extrusion, cold forming, wire drawing, deep drawing
10-100	Pure or Mixed Powders	Punching, stamping, forming, relays, switches, packings
Composites		
1-10	Friction Products, Sintered Cu brakes, Semi-metallic and Non-asbestos Pads	Aircraft, automotive and rail brake pads & clutch linings
1-30	Plastic, Rubber & Metal Composites	Gears, slides, bearings thrust washers, O-rings

DUPLEX STAINLESS STEELS

The second generation of duplex stainless steels has become a complex family of great commercial significance during the last decade. The combination of corrosion performance and advantageous mechanical properties auger well for rapid growth in applications during the next few years.

Duplex stainless steels, with a microstructure of about 50% austenite, 50% ferrite and an Mo content of up to 5%, provide an unusually good combination of properties:

- typically twice as strong as the common austenitic stainless steels;
- many of the advantages of the ferritic stainless steel, for example high resistance against chloride stress corrosion cracking;
- the range of corrosion resistance is almost as extensive as that of austenitic stainless steels.

Duplex stainless steels have a proven track record as versatile materials both in highly corrosive environments and as cost efficient engineering materials for stainless steel structures. Applications include:

- pulp & paper industry
- chemical & petrochemical industries
- hydrometallurgy
- organic acid and caustic media
- pollution control equipment
- chemical tankers
- on/off shore applications
- brewery and piping systems
- architecture

N 10276, a nickel base alloy containing 15-17% Mo, is used in the construction of seawater-based flue-gas desulphurisation plants, where the combination of seawater and sulphur-laden flue gases produce a highly corrosive atmosphere.

Use of this alloy, which performs well in the aggressive environment of the absorber towers (or scrubbers) of the FGD plant, contributes towards maintenance of removal efficiency levels of 99%, which are significantly higher than those for conventional desulphurisation methods.

London Tube tunnel linings use highly alloyed super duplex stainless steel

Seawater-based flue-gas desulphurisation plant

Molybdenum plays a vital part in everyday life, particularly in relation to many aspects of the protection of human health and the environment.

The toxicity of molybdenum is low, reducing concerns about the presence of trace amounts in water and soils which may enter the human food chain. Further, this low toxicity enables molybdenum to play a significant part in lubricants used for food processing machinery, minimising the consequences of accidental contamination.

There has been much concern about the generation of fumes when materials such as those used for carpets and furniture, made from artificial fibres, ignite. Molybdenum compounds in certain polymers have been found to be particularly good smoke suppressants.

Molybdenum-containing catalysts are used in the production of petroleum products to remove sulphur, thereby minimising emissions. This applies not only to the internal combustion engine but also to gas turbines, large combustion plants for power generation and fired heaters in the chemical, petrochemical and process industries.

Molybdenum plays a most important part in processes developed to treat pollutants, such as the desulphurisation of flue gases generated by combustion of sulphur containing fossil fuels and the cleaning of gases from the incineration of municipal and other wastes. Here, full advantage is taken of the classical role of molybdenum in enhancing the corrosion resistance of stainless steels and nickel-base alloys to withstand extreme conditions of corrosion attack.

Cost effective applications of molybdenum containing materials are demonstrable, taking advantage in design of inherent characteristics of strength, corrosion resistance and integrity.

Sponsored by IMOA and conducted in accordance with internationally accepted protocols and Good Laboratory Practice, toxicity tests have shown molybdenum oxide, ammonium dimolybdate and sodium molybdate to be non-toxic (based on EU criteria of a ‘harmful’ substance) following acute oral, inhalation and dermal exposures. These materials were also found to be non-irritating to the skin and eyes and non-sensitising.

Similar ecotoxicity tests showed pure molybdenum oxide, ammonium dimolybdate and sodium molybdate to be non-toxic to fish and daphnids following acute exposure. Algal growth was inhibited only by ammonium dimolybdate, probably due to the ammonia component rather than the molybdate ion.

The International Molybdenum Association (IMOA) was founded in 1989 and has become the focal point of promotional, statistical and technical activities for the worldwide molybdenum industry. Membership is broad based and includes producers, consumers, converters, traders and assayers. IMOA's secretariat is based in London.

IMOA's main activities currently include:

- promoting molybdenum as a material with superior properties and performance in a wide variety of metallurgical, chemical and other product applications:
- monitoring molybdenum in relation to health, safety and environmental issues; with the increasing amount of legislation in many countries relating to the use and disposal of metals and metal bearing materials, IMOA provides a centralised service including research studies on those issues that may affect the molybdenum industry;
- collecting the industry's most comprehensive historical statistics on world supply and demand of molybdenum products which are distributed to all IMOA members on a regular basis;
- organising meetings and promotional conferences beneficial to the molybdenum industry;
- preparing worldwide industry guidelines to improve the consistency and quality in sampling and assaying procedures for molybdenum products.

Background to back cover photo: Precipitation of Ammonium Polymolybdate

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OTHER IMOA PUBLICATIONS INCLUDE:

Applications of Molybdenum in Environmental & Human Health Protection

Procedure for Weighing and Sampling Molybdenite Concentrates

Procedure for Weighing and Sampling Technical Grade Molybdenum Oxide

Procedure for Weighing and Sampling Ferromolybdenum

Applications of Mo Metal and its Alloys

The Evolution of High Performance Stainless Steels

On the Internet: Database of Molybdenum in the Environment [http://www.imoa.org.uk]

IMOA

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