

NEWSLETTER



17th Annual General Meeting

This event will be kindly hosted in Shanghai by Jinduicheng Molybdenum Mining Corp, owners of the largest moly mine in China, during the week beginning 12 September 2005. Non-members wishing to attend should contact the Secretariat for further details.

HSE Management

The focus on HSE by regulatory authorities affects all metals and IMOA is not alone in spending an increasing amount of time and money to ensure that the industry it represents is ready to respond with facts and figures. IMOA has appointed a team (see photo) to implement its work programme. Sandra Carey, who has been connected with moly and IMOA for many years, will direct our activities; and technical support will be provided by Wieslaw Piatkiewicz who is employed by the Galvanizers Association and whose expertise in risk assessment will be invaluable.

IMOA's HSE Management Team: Sandra Carey and Wieslaw Piatkiewicz

To most of our readers, neither will need any introductions. Both may be contacted via the IMOA office.

Membership

Welcome to:

■ JSC Polema Corp,

a Russian company manufacturing metal powders. Its product range comprises more than 500 molybdenum product items including large sized high purity (99.90-99.96%) molybdenum sputtering targets and molybdenum metal powder.

Chemical Applications of Molybdenum

IMOA has tended to focus its market development work programme on metallurgical applications since these comprise some 80% of moly usage and appear to offer the greatest scope for increasing moly consumption.

This Newsletter comprehensively remedies the fact that an article on chemical applications is long overdue.

The author, Philip Mitchell, is Emeritus Professor of Chemistry at the University of Reading in the UK_ihe has been associated with the moly industry since the mid-1960s and is a part-time consultant to IMOA. He is responsible for compiling the Database "Mo in Relation to Health, Safety and the Environment", which may be accessed on our website.

The article which follows is an adapted version of the paper he presented in an entertaining fashion (not easy with all those complicated bonds and formulae) at the Association's Annual General Meeting in 2004.

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Chemical Applications of Molybdenum

Understanding molybdenum chemistry and applications

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Molybdenum Compounds and Applications

The purpose of this article is to describe the technical applications of molvbdenum compounds and the underlying chemistry. Important, i.e. higher volume, applications are listed in Table 1. These applications have been known for many years and are well established. Research in this area is about improving performance and developing understanding of how the compounds work. Molybdenum compounds account for ca 20% of molybdenum usage with catalysts the major application. Recent usage data for the United States are shown in Fig. 1.

The types of compound which find application are overwhelmingly molybdenum-oxygen compounds and molybdenum-sulfur compounds, see *Table 2*. However compounds of molybdenum with other elements continue to attract interest and feature in the research and patent literature. Compounds are listed in *Table 2* with an indication of actual use (italicised) or proposed use and numbers of US patents since 1976.

Basic Molybdenum Chemistry

Molybdenum is an element of the second transition series in Group 6 of the Periodic Table between chromium and tungsten. Chemically molybdenum resembles tungsten much more than chromium. For example, the highest oxidation state (VI) of molybdenum and tungsten (molybdates and tungstates) is much less oxidising than chromium(VI) (chromate and dichromate).

(chromate and dichromate).

Table 1 Some Uses of Molybdenum Compounds		
catalysts	MoO3, molybdates, e.g. iron and bismuth molybdates molybdenum disulfide	
lubricants	molybdenum disulfide molybdenum-sulfur complexes, e.g with dithiocarbamate (R2NCS2 ⁻) and dithiophosphate ((R0)2PS2 ⁻).	
corrosion inhibitors	sodium molybdate	
paints, and surface coatings	molybdates, e.g. zinc molybdate	
smoke suppressors	MoO3, ammonium octamolybdate	
pigments	ammonium and alkylammonium octamolybdates, phosphomolybdic acid	
ceramics	molybdenum disilicide	
nanomaterials	molybdenum disulfide, molybdenum carbide	
agriculture	molybdates	

The outstanding feature of molybdenum is its extraordinary chemical versatility:

- oxidation states from –II to VI;
- coordination numbers from 4 to 8;
- varied stereochemistry;
- the ability to form compounds with

most inorganic and organic ligands, with a particular preference for oxygen, sulfur, fluorine and chlorine donor atoms;

formation of bi- and polynuclear compounds containing bridging oxide or chloride ligands and/or molybdenummolybdenum bonds.

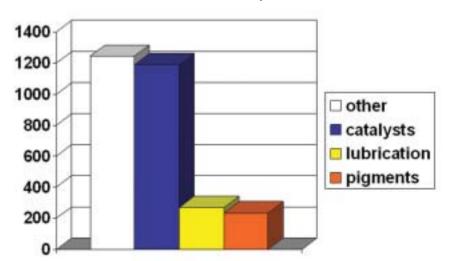


Fig. 1 Molybdenum chemicals usage in metric tonnes (1000 kg) contained Mo, United States 2002. Data from the US Geological Survey Minerals Division. http://minerals.usgs.gov/minerals/pubs/commodity/molybdenum/molybmyb02.pdf

Entering Molybdenum Chemistry– Making Molybdenum Compounds

Compounds commonly used as starting compounds in preparative molybdenum chemistry are molybdenum trioxide, and ammonium and sodium molybdates.

The preparative chemistry of molybdenum is summarised in *Fig. 2* starting with molybdenum disulfide, the principal ore of molybdenum. Molybdenum disulfide is chemically unreactive: we enter molybdenum chemistry through molybdenum trioxide, prepared by roasting molybdenum disulfide in air. Reactions of molybdenum trioxide are shown in *Fig. 2.*

Dissolution in aqueous sodium hydroxide or ammonia giving simple molybdate salts and polymolybdates which may be crystallised (see later).

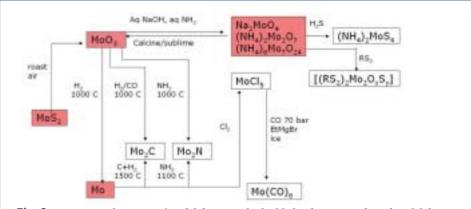


Fig. 2 Preparative chemistry of molybdenum. The highlighted compounds and molybdenum metal are those which find high volume applications.

Calcination of an ammonium molybdate giving a sublimed, pure molybdenum trioxide.

Reduction with hydrogen to molybdenum metal.

Reactions with carbon monoxide or carbon and ammonia giving molybdenum carbide and nitride.

Preparation of molybdenum pentachloride and molybdenum hexacarbonyl. The pentachloride rapidly hydrolyses in ambient air and is too reactive to find wide application. Molybdenum hexacarbonyl has an extensive substitution chemistry.

Preparation of molybdenum-sulfur compounds by reaction with hydrogen disulfide or organo-sulfur compounds.

Higher Oxidation States

The commonly encountered compounds of molybdenum in its applications are molybdenum trioxide and molybdates (oxidation state VI) and molybdenum disulfide (oxidation state VI) (see *Table 1*).

Molybdates and polymolybdates

These are compounds of molybdenum(VI): sodium molybdate, Na²MoO⁴; ammonium dimolybdate, (NH⁴)²Mo²O⁷, ammonium heptamolybdate, (NH⁴)⁶Mo⁷O²⁴.4H²O and ammonium octamolybdate, (NH⁴)⁴Mo⁸O²⁶. They are readily available commercially and are the starting point for the preparation of many other molybdenum compounds.

Sodium molybdate crystals contain the discrete tetrahedral [MoO₄]^{2.} ion. The polymolybdates consist of linked polyhedra containing six- and four-, and less commonly five-coordinate molybdenum(VI).

Molybdenum trioxide and the molybdates of colourless cations are themselves colourless. Blue or green colours are due to the presence of reduced impurities except for those molybdates where the cation is coloured, e.g. violet cobalt(II) molybdate, CoMoO₄, and green nickel(II) molybdate, NiMoO₄

In aqueous solution molybdate and polymolybdate ions are in rapid equilibria; the species depends on the pH and the concentration,see **Table3**. The molybdate species in aqueous solutions of molybdenum(VI) (*speciation*)are listed in **Table 3**.

Table 2	Mo compounds—Partner Element(a) Applications(b)
	Patents (c)

В	С	N	0	F
Mo2B	Mo ₂ C	Mo2N	MoO₃,	MoF₀
catal. ceram.	catal.	catal.	molybdates catal. corros. pigment smoke	catal.
168	817	299	3671	89
	Si	Р	S	CI
	MoSi ² ceram.	MoP catal. glasses	MoS₂ catal. lub.	MoCl₅ catal.
	1827	15	4381	244
			Se	Br, I (=X)
			MoSe₂ Batt.	MoBr4, MoI3
			30	
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(a) Listed in Periodic Table order. (b) batt., batteries and electrode materials; catal., catalyst; ceram., ceramic; corros., corrosion inhibitor; lub., lubricant; pigment, pigment; smoke, smoke suppressant.
 Significant uses are italicised. (c) Figures in red are the numbers of patents in the US Patent data base, 1976 to present (http://www.uspto.gov/patft/index.html).

Table 3 Mo(VI) Species in Aqueous Solution		
рΗ	Mo concentration/ mol I ⁻¹	Mo(VI) species
>7	all	[MoO4] ²⁻
5–6	>10 ⁻³ mol l ⁻¹	[Mo7O24] ⁶⁻
3–5	>10 ⁻³ mol l ⁻¹	[Mo ₈ O ₂₆] ⁴⁻
0.9	>10 ⁻³ mol l ⁻¹	MoO3 precipitates

Which compounds crystallise from solution depends on the conditions: concentration and pH. To prepare sodium molybdate, Na2MoO4.2H2O molybdenum trioxide is dissolved in sodium hydroxide solution at 50-70 ^oC. The solution is filtered and the filtrate is crystallised in a batch crystalliser. The hydrated salt is dehydrated at 100 °C. Ammonium dimolybdate, (NH4)2M02O7, is prepared by dissolving MoO₃ in aqueous ammonia solution and crystallising the solution at ca 100 °C by flash evaporation. The structure of ammonium dimolybdate, determined by X-ray crystallography on crystals from the manufacturing plant, consists of infinite chains of pairs of edge-shared MoO6 octahedra, adjacent pairs being linked by MoO4 tetrahedra with the chains having equal numbers of octahedra and tetrahedra. The structure is quite different from that of dichromate which contains discrete [Cr₂O₇]²⁻ ions. Ammonium heptamolybdate, (NH4)6M07O24.4H2O, is prepared by crystallising a solution of MoO₃ in aqueous ammonia of the requisite NH₃/Mo/H₂O stoichiometry at ambient temperature. The structure comprises linked [MoO6] octahedra only. The alkylammonium molybdates are salts-not complexes; tetrakis (isopropylammonium)octamolybdate (VI), $[C_3H_{10}N]_4[MO_8O_{26}]$ is typical.

Heteropolymolybdates

The heteropolymolybdates consist of $[MoO_6]$ octahedra incorporating atoms of a different element, the heteroatom. The heteroatoms are completely surrounded by the oxygen atoms of the $[MoO_6]$ octahedra. The resulting coordination of the heteroatom may be tetrahedral or octahedral. The 12-molybdo species, $[X^{+n}Mo_{12}O_{40}]^{<8\cdot n}$; is an important group

with tetrahedrally coordinated heteroatoms (X). An example is 12-molybdophosphoric acid H₃[PMo₁₂O₄₀].28 H₂O, prepared by dissolving molybdenum trioxide in phosphoric acid; it is yellow and readily soluble in water.

Lower Oxidation States

Molybdates(VI) unlike chromates(VI) are not strong oxidising agents: much of the familiar chemistry of molybdenum is that of the VI and V oxidation states. The products of the reduction of molybdate in aqueous solution depend on the pH and the reducing agent. In alkaline solution molybdates are reduced by, e.g. sodium dithionite, to molybdenum blues, mixed Mo(VI)-Mo(V) oxides. In dilute hydrochloric and sulfuric acids tin(II) chloride effects reduction to brown molybdenum(V) species; in concentrated hydrochloric acid the green $[MoOCl_5]^2$ - species is formed. With a more powerful reducing agent, e.g. zinc amalgam, reduction proceeds to hydrated molybdenum(III) species. Typical reduction potentials (in volts) in acidic solution are for Mo(VI)/Mo(V), 0.50, and for Cr(VI)/Cr(III), 1.35. The more positive is the potential, the more oxidising is the couple.

Compounds of molybdenum(II) and lower oxidation states are stabilised by Mo-Mo bonds as in molybdenum(II) acetate, Mo²(CH³CO²)⁴, and molybdenum(II) chloride, Mo⁶Cl¹², and by unsaturated ligands, for example, molybdenum(0) hexacarbonyl, Mo(CO)⁶. There is an extensive and important organometallic chemistry of molybdenum, i.e. compounds with Mo-C bonds with, e.g. cyclopentadiene and benzene.

Molybdenum– sulfur Compounds

In addition to its affinity for oxygen, molybdenum in its higher oxidation states, (III) to (VI), has an appreciable affinity for sulfur, a property which is important in its biochemistry and in a number of applications. The affinity of molybdenum for sulfur is illustrated by its occurrence as the sulfide ore, MoS₂, and in molybdoenzymes; its precipitation in qualitative analysis as a sulfide rather than as a hydroxide or

Catalyst	Application	Reaction	Importance
Sulfided Co-Mo or Ni-Mo on alumina	Hydrotreating, hydrodesulfurisation	Remove sulfur from crude petroleum	Oil and petroleum refining
Bi-Mo oxides	Propene selective oxidation, ammoxidation	Synthesis acrolein, acrylonitrile	Polymers and plastics
Mo-V oxides	Acrolein oxidation	Synthesis acrylic acid	Polymers and plastics
Fe-Mo oxides	Methanol oxidation	Synthesis formaldehyde	Formalin, polymers, resins
Mo oxide on alumina	Olefin metathesis	Propene to ethene butene	Olefin and synthesis
Mo complexes	Epoxidation	Olefin to epoxide	Polyether synthesis
Heteropolyacids— phosphomolybdate	Propene hydration	Propene to alcohol	Alcohols synthesis

Table 4 Molybdenum in catalysts

hydrated oxide. Molybdenum disulfide is black.

It is unreactive towards water and acids and alkalis. However, molybdenum disulfide and other Mo-S compounds oxidise when heated in air to molybdenum trioxide. Because of the unreactivity of molybdenum disulfide, Mo-S compounds are made via reaction with molybdates as in the preparation of hydrodesulfurisation catalysts (see later). Molybdenum disulfide is used, per se, as a dry lubricant (see later).

Molybdenum forms complexes with sulfide ([MoS₄]²⁻) and many organosulfur ligands. These compounds unlike their oxygen counterparts are often brightly coloured, e.g. [MoS₄]²⁻ is deep orange-red. The dithiocarbamates and dithiophosphates are applied as oil soluble lubricant additives (see later).

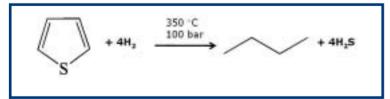
Applications

Molybdenum Compounds in Catalysis

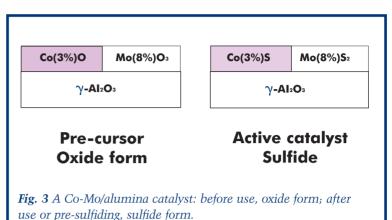
The function of a catalyst is both to speed up a chemical reaction and to steer it towards a desired product, e.g. an oxygenated organic compound rather than carbon dioxide and water. Catalysts having molybdenum as a component are listed in *Table 4*. We see from *Table 4* that it is Mo-O compounds which find application in high volume catalysis. Sulfide catalysts are derived from the oxides.

Molybdenum in hydrodesulfurisation catalysts

Removal of sulfur compounds from gasoline and diesel is driven by ever more stringent legislation since during combustion the sulfur compounds oxidise to sulfur dioxide, the source of acid rain. They are also potent poisons of auto-exhaust catalysts. The process is *catalytic hydrodesulfurisation*—removal of sulfur by reaction of the compound with hydrogen—for which molybdenum-based catalysts are essential. Recalcitrant compounds are thiophene and benzothiophenes. The reaction of thiophene with hydrogen is typical:



The catalyst, see *Fig. 3*, comprises cobalt (3 wt-%) and molybdenum (8 wt-%) as sulfides supported on alumina. It is prepared by impregnating γ -alumina with ammonium molybdate and cobalt(II) nitrate solutions followed by drying and calcination. The molybdenum and cobalt sulfides are formed when the catalyst is pre-sulfided or used. The active component is molybdenum disulfide. Cobalt (a promoter) is added to increase the activity. Alumina provides surface area (ca 250 m² g⁻¹) by dispersing the cobalt and molybdenum.



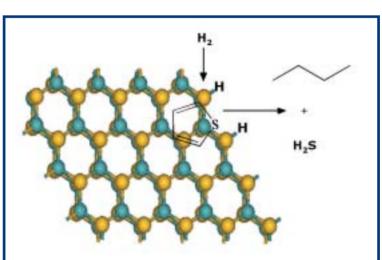
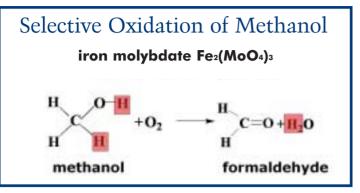


Fig. 4 Hydrodesulfurisation of thiophene catalysed by molybdenum disulfide: Mo atoms, green, S atoms yellow. The catalyst dissociates H_2 molecules into H atoms which react with adsorbed thiophene yielding butane and hydrogen sulphide.

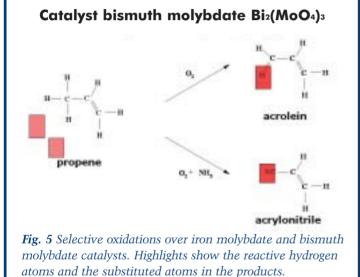
The active catalyst consists of hexagonal slabs of molybdenum disulfide, sections of a molybdenum disulfide layer, *Fig. 4.* The utility of molybdenum in this catalysis derives from the layer structure molybdenum disulfide. (The same is true for tungsten disulfide which also catalyses hydrodesulfurisation.) The catalytic sites are at the slab edges (where cobalt atoms, not shown, are also located). A reactant molecule, thiophene, is shown in *Fig. 4* adsorbed near an edge site and reacting with hydrogen atoms to give, ultimately, butane and hydrogen sulfide. We require of molybdenum disulfide the ability to dissociate hydrogen molecules, adsorb reactant molecules, and release sulfur as hydrogen sulfide reversibly.

Molybdenum in selective oxidation catalysts

The technically important reactions of methanol oxidation to formaldehyde and propene to acrolein and acrylonitrile are shown in *Fig. 5.*



Selective Oxidation of Propene



In these selective oxidations the slow step, which controls the overall reaction rate and which it is desired to catalyse, is activation of the first C-H bond. With these two-component catalysts, the first step, breaking the C-H bond, is catalysed by the more basic oxide, e.g. bismuth oxide. Molybdenum is involved in the next step— activation of a second hydrogen and insertion of an oxygen atom into the organic molecule. In this step molybdenum is reduced. Reduced molybdenum is reoxidised by oxygen from the feed. The catalysis depends on the ability of oxomolybdenum species to cycle between the VI and IV oxidation states, in the process releasing and transferring an oxygen atom:

 $Mo(VI)O_2 \leftrightarrow Mo(IV)O + O$

Note that the inserted oxygen comes from the lattice of the catalyst; there is no direct reaction between the organic compound and an oxygen molecule. The same molybdenum chemistry—reduction of molybdenum accompanied by oxygen atom transfer—also operates with oxomolybdenum enzymes, e.g. xanthine oxidase.

Other applications of molybdenum compounds in catalysis

A number of molybdenum compounds find application in homogeneous catalysis: e.g. in epoxidation (see *Table 4*), olefin and acetylene metathesis ($Mo(CO)_6$), olefin polymerisation ($MoCl_5$ and triethylaluminium in Ziegler Natta type catalysts).

Molybdenum-sulfur Compounds in Lubrication

Molybdenum disulfide is used as a dry lubricant in, e.g. greases, dispersions, friction materials and bonded coatings. Molybdenum-sulfur complexes may be used in suspension but more commonly dissolved in lubricating oils at concentrations of a few percent.

The ability of molybdenum disulfide to function as a lubricant is intimately related to its layer structure, *Fig.6.* A layer of molybdenum atoms is sandwiched between two layers of sulfur atoms.

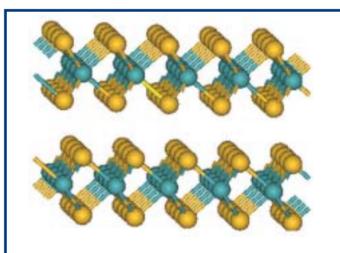


Fig. 6. A side view of the layer structure of molybdenum disulfide. The green spheres represent molybdenum atoms and the yellow spheres sulphur. The outer layers of sulfur atoms bind to each metal surface. Contact between the metal surfaces is prevented.

When molybdenum disulfide is dispersed between two metal surfaces a layer binds to each metal surface through the sulfur atoms. Then the asperities (surface irregularities on the metals) are prevented from coming into contact. Sliding contact is between the outer layers of sulfur atoms which are only weakly interacting. The surfaces are therefore able to slide easily relative to one another.

Compounds typically used as oil soluble additives are shown in *Fig.* 7. They are used dissolved in lubricating oils. At a hot surface—the interfacial region between metals in rubbing contact—the complexes decompose to molybdenum disulfide or to a polymeric protective film. These compounds are also of some benefit in protecting the oil against oxidation; they are anti-oxidants.

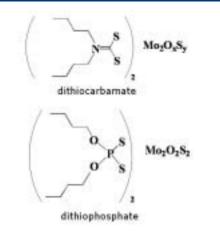


Fig. 7. Molybdenum-sulfur compounds used as soluble lubricating oil additives.

Molybdenum compounds as corrosion inhibitors and in paints

The use of molybdates as corrosion inhibitors and in paints is summarised in Table 5. Soluble molybdates, e.g. sodium molybdate, are used in solution in central heating systems and motor engine coolants. The insoluble molybdates are applied as paint primers and as paints. Molybdates, unless combined with a coloured cation or mixed with a coloured compound, are white and so have application as white pigments. For example zinc molybdate which is non-toxic and an excellent corrosion inhibitor. The orange colour of the molybdenum orange pigment is due to the presence of chromate. This pigment consists of lead molybdate, chromate and sulphate in a mixed crystal system. Lead chromate is yellow whereas the molybdated chromes are bright orange. The colour change is due to a modification of the crystal structure of lead chromate when crystallised with molybdate.

The ability of molybdate to inhibit corrosion is demonstrated in standard tests in which steel plates are exposed to a salt spray. Molybdate is seen to prevent surface pitting of test pieces (e.g., see http://www.pcimag.com). Molybdate prevents corrosion through its ability to be adsorbed by a metal oxide layer, filling gaps and so promoting the formation of an adherent oxide layer. Corrosion of the underlying substrate is prevented-it becomes passivated.

Molybdates as smoke suppressants

Ammonium octamolybdate and molybdenum trioxide are used as smoke suppressants in, for example, PVC cabling. They are thought to act by undergoing reduction to lower valent molybdenum, e.g. molybdenum dioxide, which then cross links the plastic to form a char. Molybdenum stabilises the char so preventing the formation of smoke particles.

Molybdenum disilicide in ceramics and advanced materials

Because of its high melting point (2030 °C) and excellent oxidation resistance molybdenum disilicide, MoSi2, finds application as a specialised ceramic in: heating elements, air furnaces; gas burners; diesel engine glow plugs; molten metal lances; aerospace, gas turbine engines, outer seal.

Molybdenum compounds in agriculture and biology

Molybdenum is an essential trace element-in plants, in enzymes which catalyse nitrogen fixation (nitrogenase) and nitrate reduction (nitrate reductase); in animals, in enzymes involved in, e.g., nitrogen metabolism (e.g., xanthine oxidase) and sulphur metabolism (sulfite oxidase). Some soils, especially acid soils require supplemental molybdenum for healthy plant life. For human beings molybdenum features as a component of over-the-counter vitamin and mineral supplements. Molybdenum is non toxic for humans.

The vital role of molybdenum in biology derives from its affinity for sulfur, its finely balanced oxidation states, and its ability in its higher oxidation states to transfer oxygen atoms.

Outlook

We have seen that molybdenum has a rich and varied chemistry and applications in catalysis, lubrication, corrosion inhibition, paints and pigments which reflect this chemistry. Molybdenum is an essential trace element in biology-vital for life processes. Unlike some metals molybdenum is not toxic towards human beings. Molybdenum chemistry is an active research area, both in fundamentals and applications. Faced with a chemical challenge it is always worth 'thinking molybdenum'.

Further Information

Fundamentals of molybdenum chemistry are presented in inorganic chemistry texts: Cotton, F.A., and G. Wilkinson, Carlos A. Murillo and Manfred Bochmann, Advanced Inorganic Chemistry, Sixth Edition, 1999, John Wiley, New York.

Greenwood, N.N., and A. Earnshaw, Chemistry of the Elements, Second Edition 1997, Butterworth, London. Fundamental chemistry and applications are covered in Ullmann's Encyclopedia of Industrial Chemistry, VCH Weinheim 1990 *Vol. A 16: Molvbdenum and Molvbdenum* Compounds.

The chapter by E.R. Braithwaite in a *multi-author publication is an excellent* account of molybdenum applications: Braithwaite, E.R. and J. Haber (eds.), Molybdenum: An Outline of its Chemistry and Uses, 1994, Elsevier, Amsterdam.

Steel, aluminium, copper		
Central heating systems	Sodium molybdate	
Automobile engine coolant		
Paints	Zinc, calcium, strontium molybdate	
Plastics	Molybdenum orange: lead molybdate plus lead chromate	
Rubber	Phosphomolybdates	
Ceramics	7	

Table 5 Molybdenum-based Corrosion Inhibitors and Paints



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