

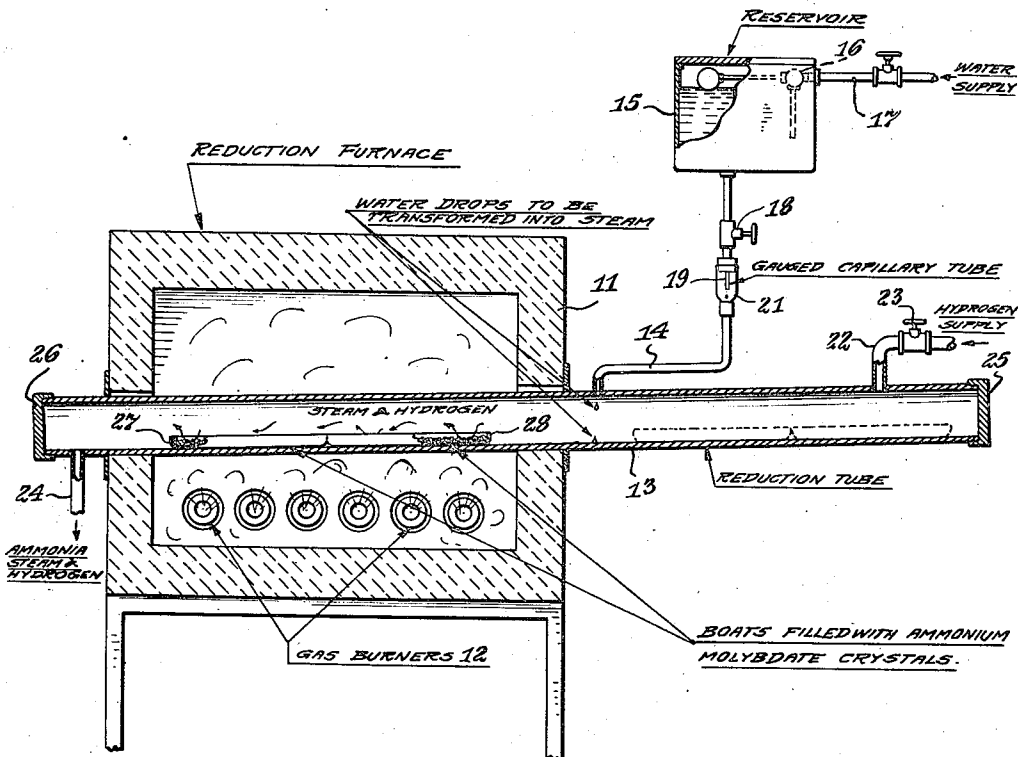
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REDUCTION OF AMMONIUM MOLYBDATE

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REDUCTION OF AMMONIUM MOLYBDATE

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This invention relates to the manufacture of molybdenum, and more particularly to a method and apparatus for reducing ammonium molybdate for that purpose.

The principal object of my invention, generally considered, is the shortening and otherwise improving on the manufacture of molybdenum from ammonium molybdate.

Another object of my invention is the reduction of ammonium molybdate to molybdenum, employing hydrogen instead of other reducing agent, but allowing some of the ammonia generated from the ammonium molybdate to assist in the reduction operation, and employing steam to control the reaction and prevent a runaway-reaction.

A further object of my invention is the production of molybdenum by first heating ammonium molybdate to break it down to molybdenum trioxide, ammonia and water, increasing the temperature and allowing the generated ammonia to reduce some of the trioxide to dioxide, admitting steam to drive off the surplus ammonia, admitting hydrogen to reduce the remaining molybdenum trioxide and the dioxide to molybdenum, with the steam controlling the reaction, cutting off the steam, increasing the hydrogen flow, raising the temperature, and holding an increased temperature in this stream of hydrogen until practically all of the material has been reduced to molybdenum.

Other objects and advantages of the invention, relating to the particular arrangement and construction of the various parts, will become apparent as the description proceeds.

In the drawing:

The single figure is a sectional view of a furnace and associated apparatus for reducing ammonium molybdate to molybdenum.

Formerly ammonium molybdate was reduced, by the Westinghouse Lamp Co., to molybdenum by first using illuminating gas to effect a partial reduction and then employing hydrogen to complete the reduction thereof, the schedule lasting about sixteen hours. It is found, however, that the use of carbon-containing material, such as illuminating gas, might leave some carbon in the reduced metal, and the employment of hydrogen throughout was not entirely safe because the reaction is exothermic and liable to "run away" or proceed too rapidly, with the production of metal having hard cones or clinkers, designated as "cony" metal.

In accordance with my invention I have avoided the danger of carbonizing the metal by

eliminating the use of illuminating gas, and the danger of a "run-away" reaction with hydrogen by admixing steam therewith in the early stages of the reaction, while at the same time allowing the generated ammonia to effect some of the reduction and thereby save that amount of hydrogen.

Referring to the drawing in detail, like parts being designated by like reference characters, there is shown a furnace 11 which, in the present instance, is fired by gas burners 12, although other heating means may be employed, if desired. Through the furnace runs a slightly inclined reduction tube 13, which may be formed of relatively refractory material, such as nichrome, and connected to said tube, and exterior of said furnace, is a pipe 14 by means of which water may be introduced for the formation of steam.

The water is supplied to the pipe 14 from a reservoir 15 and kept at the desired level by a float-controlled valve 16 in the water supply pipe 17. The flow of water from the reservoir is controlled by a valve 18 admitting water through gauged capillary tube 19 into a transparent connection 21, permitting observation of the flow of water.

The hydrogen supply passes to the reduction tube 13 through pipe 22 controlled by valve 23. The exhaust from the reduction tube passes out through relatively small pipe 24, which may, at times, be connected to the hydrogen supply line to salvage hydrogen unused in the furnace, after condensation therefrom of the steam. The ends of the reduction tube 13 are normally closed by caps 25 and 26.

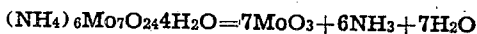
I will now describe a preferred reduction schedule of ammonium molybdate to molybdenum, it being understood, however, that said schedule is merely illustrative and changes may be made within the broad scope of my invention.

The ammonium molybdate, probable composition, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, in the form of crystals, is placed in boats, 27 and 28, desirably formed of refractory material such as nickel, preferably about $2\frac{1}{2}$ kilograms per boat, the material being spread out to expose as much surface as possible.

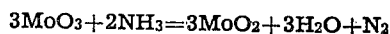
As illustrated in the drawing, the boats are of sufficient size so that when positioned, as shown in full lines, they extend from one end to the other of the heated portion of the reduction tube. The filled boats may be first introduced into the cold or right hand end portion of the tube, through the opening shown closed by the cap 25, and

pushed into the furnace to the position illustrated.

Considering that the operation starts with the reduction tube at a temperature of about 180° C., the temperature is raised over a period of one-half hour to about 430° C. During this time, the ammonium molybdate begins to break down to molybdenum trioxide, ammonia and water, the reaction being:

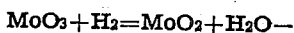


The temperature of the reduction tube is then increased from about 430° to about 630° C. over a period of about one hour. At 430° C. the molybdate breaks up more rapidly and the reaction is about completed by the time the furnace is up to 630° C. The generated ammonia reduces from about one-third to one-half of the molybdenum trioxide to molybdenum dioxide, the formula being:



After holding for about one-quarter of an hour at about 630° C., the valve 18 is opened to admit water to the capillary tube 19, from whence it flows to the reduction tube for conversion to steam. The flow of water is at the rate of about 12 cu. cm. per minute, the function of the generated steam being to clear the tube of ammonia prior to admission of the hydrogen and to form a diluting agent for the hydrogen to prevent a "run away" reducing action.

After about another quarter hour, the valve 23 is opened admitting hydrogen to the reduction tube at the rate of about 30 cu. ft. per hour. This mixes with the generated steam and a controlled reaction occurs whereby the molybdenum trioxide is converted to molybdenum dioxide, and some of the latter is converted to molybdenum, the reactions being as follows:



Inasmuch as the surplus hydrogen is free from ammonia and other contaminating agents, except steam, it is desirably returned to the hydrogen supply line for re-use after condensation of the steam.

After another half hour of operation at about 630° C. the water supply is shut off, as the reaction will have proceeded to such a point where most of the molybdenum trioxide has been converted to the dioxide and the danger of a "run-away" is past.

After further operation for about three-quarters of an hour the rate of hydrogen flow is desirably increased from 30 to 50 cu. ft. per hour. This is at a time when the reaction has progressed so that there may be a considerable reduction of the material near the inlet end, with a lesser amount of reduction toward the outlet end. This increase in flow counteracts the tendency toward too rapid reduction at the inlet end, cooling the charge at this point, while providing the needed greater hydrogen concentration near the outlet end.

After continued operation for about another half hour, the temperature of the reduction tube is gradually increased so that it reaches about 1040° C. in about one and three-quarters hours. It is kept at this increased temperature for about three and one-half hours more, after which all of the charge should be converted to the metallic molybdenum and the process is complete.

The foregoing may be summarized by the following table:

Hours	O'clock	Furnace temperature	
0	8	180° C	
1/2	8:30	430	Molybdate decomposes, NH ₃ reduces some MoO ₃ to MoO ₂ . 12 cc. H ₂ O per min. NH ₃ clears. 30 ft. of H ₂ per hr. MoO ₃ and some MoO ₂ reduced. Water off. 50 ft. of H ₂ per hr.
1 1/2	9:30	630	
1 3/4	9:45	630	
2	10:00	630	
2 1/2	10:30	630	
3 1/2	11:15	630	
3 3/4	11:45	Raise	
5 1/2	1:30	1040	
9	5:00	Off	Remainder of MoO ₃ reduced to Mo.

From the foregoing it will be seen that I have not only shortened the schedule from 16 to 9 hours and provided for the production of better metal by the elimination of clinkers or cones, but I have made it possible to salvage nearly all of the unused hydrogen passed through the furnace, thereby effecting a further saving.

In order to convert an old furnace to one which may be used for practicing my invention, it is merely necessary to tilt the furnace, or the reduction tube thereof, toward the exit end and provide for a water connection such as previously described.

Although I have described the completion of reduction to molybdenum dioxide by hydrogen, it will be understood that this reduction may be practically completed by ammonia, as by introducing such from an outside source. It will also be understood that although I have described the use of steam for slowing down the reducing action of hydrogen, yet any inert gas, such as nitrogen, may be employed for the purpose.

Although preferred embodiments of my invention have been disclosed, it will be understood that modifications may be made within the spirit and scope of the appended claims.

I claim:

1. The method of reducing ammonium molybdate, comprising heating to break it down, allowing the generated ammonia to reduce some to molybdenum dioxide, admitting a reducing gas to practically complete the reduction to molybdenum dioxide, admitting an inert gas, admitting hydrogen, cutting off the inert gas and raising the temperature and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

2. The method of reducing ammonium molybdate, comprising heating to break it down to molybdenum trioxide, ammonia, and water, increasing the temperature, allowing the ammonia to reduce some of the molybdenum trioxide to molybdenum dioxide, admitting steam to drive off the surplus ammonia, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, with the steam controlling the reaction, cutting off the steam after the reaction has progressed sufficiently so that nearly all said trioxide has been reduced to dioxide and no runaway will occur, increasing the flow of hydrogen and raising the temperature, and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

3. The method of reducing ammonium molybdate, comprising heating to about 430° C. to begin to break it down to molybdenum trioxide, ammonia and water, increasing the temperature, allowing the ammonia to reduce some of the molybdenum trioxide to molybdenum dioxide, ad-

mitting steam to drive off the surplus ammonia, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, with the steam controlling the reaction, cutting off the steam after the reduction has progressed sufficiently so that nearly all of said trioxide has been reduced to dioxide and no runaway reaction will occur, increasing the flow of hydrogen, and raising the temperature until substantially all the dioxide has been reduced to molybdenum.

4. The method of reducing ammonium molybdate, comprising heating to begin to break it down to molybdenum trioxide, ammonia and water, increasing the temperature to about 630° C., allowing the generated ammonia to reduce some of the molybdenum trioxide to molybdenum dioxide, admitting steam to drive off the surplus ammonia, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, with the steam controlling the reaction, cutting off the steam after the reduction has progressed sufficiently so that nearly all of said trioxide has been reduced to dioxide and no runaway reaction will occur, increasing the flow of hydrogen, and raising the temperature and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

5. The method of reducing ammonium molybdate comprising heating to begin to break it down, increasing the temperature, allowing the generated ammonia to reduce some to molybdenum dioxide, admitting water at the rate of about twelve cubic centimeters per minute to form steam to drive off the surplus ammonia, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide with the steam slowing down the reaction, cutting off the steam after the reduction has progressed sufficiently so that nearly all of said trioxide has been reduced to dioxide and no runaway reaction will occur, increasing the flow of hydrogen, and raising the temperature and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

6. The method of reducing ammonium molybdate comprising heating to begin to break it down, increasing the temperature, allowing the generated ammonia to reduce some to molybdenum dioxide, admitting steam, admitting hydrogen at the rate of about thirty cubic feet per hour to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, cutting off the steam, and raising the temperature and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

7. The method of reducing ammonium molybdate, comprising heating to begin to break it down, increasing the temperature, allowing the generated ammonia to reduce some to molybdenum dioxide, admitting steam, admitting hydrogen at a relatively low rate to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, cutting off the steam, increasing the rate of hydrogen flow to about fifty cubic feet per hour and raising the temperature and holding the material at such temperature until substantially all the dioxide has been reduced to molybdenum.

8. The method of reducing ammonium molybdate comprising heating to begin to break it down, increasing the temperature, allowing the generated ammonia to reduce some to molybdenum

dioxide, admitting steam, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, cutting off the steam, increasing the flow of hydrogen, raising the temperature until it reaches about 1040° C., and holding at said temperature until substantially all the dioxide has been converted to molybdenum.

9. The method of reducing ammonium molybdate, comprising placing the same as crystals in boats, placing said boats in the reduction tube of a furnace, raising the temperature of said tube from 180° C. to 430° C. to cause the ammonium molybdate to begin to break down to molybdenum trioxide, ammonia and water, increasing the temperature to 630° C., the generated ammonia reducing some of the molybdenum trioxide to molybdenum dioxide, admitting water at the rate of twelve cubic centimeters per minute to form steam to drive off the surplus ammonia, admitting thirty cubic feet per hour of hydrogen to reduce the balance of the molybdenum trioxide to molybdenum dioxide, with the steam controlling the reaction, the surplus hydrogen being returned to the line because it is free from ammonia, shutting off the water, increasing the rate of hydrogen flow to fifty cubic feet per hour, raising the temperature of operation so that it reaches 1040° C. in one and three-quarter hours, and holding the material at said last-mentioned temperature so that all is converted into molybdenum.

10. The method of reducing ammonium molybdate, comprising placing about 2½ kilograms of the same as crystals in each of two nickel boats, placing said boats in the reduction tube of a furnace, raising the temperature of said tube from 180° C. to 430° C. over a period of one-half hour to cause the ammonium molybdate to begin to break down to molybdenum trioxide, ammonia and water, increasing the temperature to 630° C. over a period of one hour, the generated ammonia reducing some of the molybdenum trioxide to molybdenum dioxide, admitting water at the rate of twelve cubic centimeters per minute to form steam after one-quarter hour operation at 630° C. to drive off the surplus ammonia, admitting thirty cubic feet per hour of hydrogen after one-quarter hour further operation, to reduce the balance of the molybdenum trioxide to molybdenum dioxide, with the steam controlling the reaction, the surplus hydrogen being returned to the line because it is free from ammonia, shutting off the water after another half hour of operation, increasing the rate of hydrogen flow, after another three-quarter hour operation, to fifty cubic feet per hour, raising the temperature after another half hour of operation so that it reaches 1040° C. in one and three-quarter hours, and holding the material for about three and one-half hours more at said last-mentioned temperature so that all is converted into molybdenum.

11. The method of reducing ammonium molybdate, comprising heating to begin to break it down to molybdenum trioxide, ammonia and water, increasing the temperature, allowing the ammonia to reduce some of the molybdenum trioxide to molybdenum dioxide, admitting more ammonia to practically complete the reduction to molybdenum dioxide, admitting nitrogen, admitting hydrogen to reduce the remainder of the molybdenum trioxide to molybdenum dioxide, with the nitrogen controlling the reaction, cutting off the nitrogen after the reduction has progressed sufficiently so that no runaway reaction will occur,

and raising the temperature until substantially all the dioxide has been reduced to molybdenum.

12. Apparatus for manufacturing molybdenum, comprising a furnace, an inclined reduction tube of refractory material passing into and adapted to be heated by said furnace, means for either closing the ends of said tube or opening to admit material to be reduced at the high end

and withdraw reduced material at the low end, a connection for introducing graduated amounts of water to said tube adjacent the high end, a connection for introducing hydrogen to said tube adjacent the high end, and a connection for withdrawing surplus hydrogen from said tube adjacent the low end, for return to the supply.

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