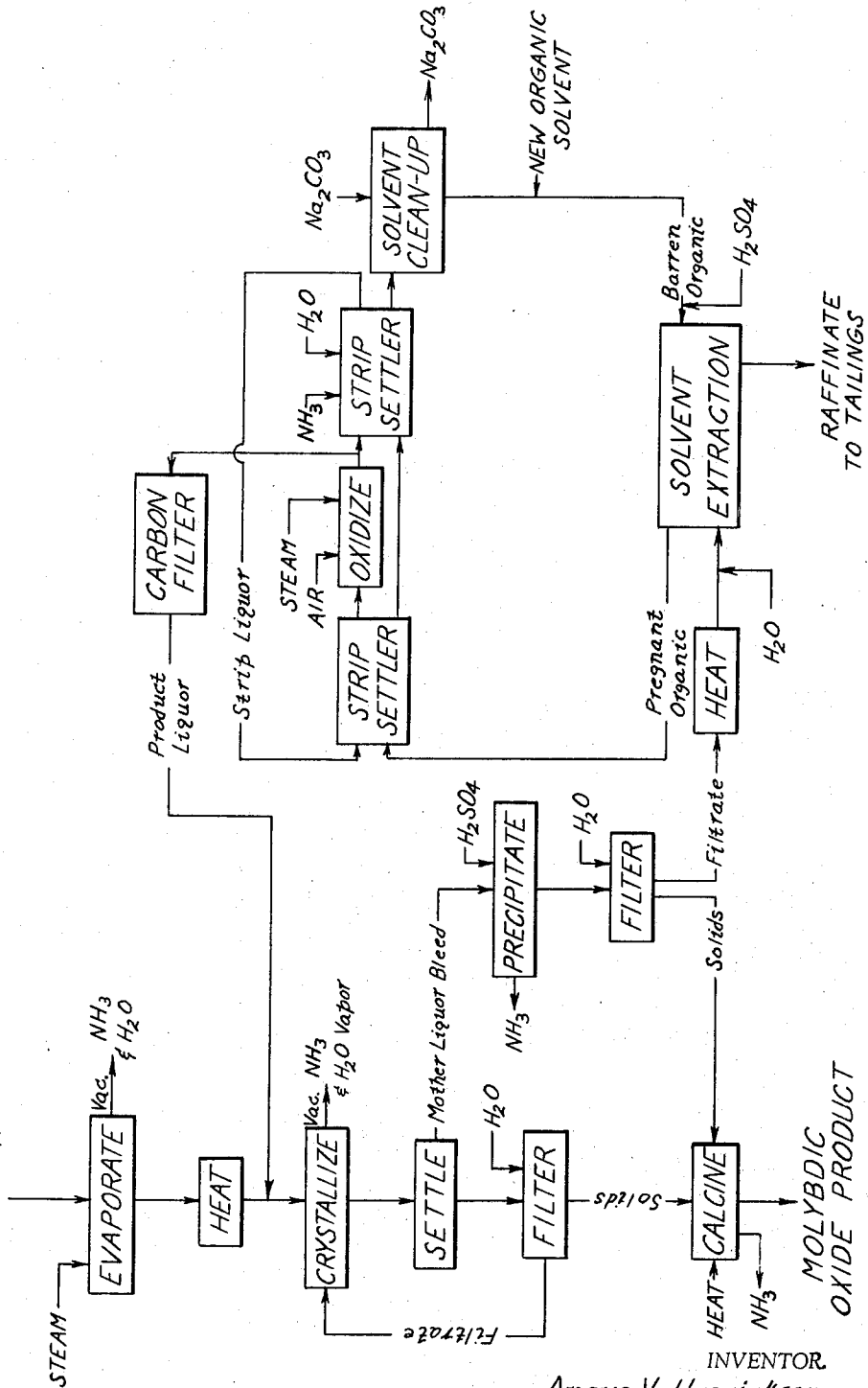


AMMONIUM MOLYBDATE
AND
AMMONIUM SULFATE
SOLUTION

[illegible]

SETTLE - Mother Liquor B



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3,357,821

PROCESS FOR EXTRACTING METAL VALUES
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 York, N.Y., a corporation of New York
 Filed Mar. 24, 1965, Ser. No. 442,408
 29 Claims. (Cl. 75—103)

The present invention relates generally to hydrometallurgical processes for recovering molybdenum values from molybdenum bearing minerals, and more particularly to novel continuous evaporation-crystallization, precipitation, and solvent extraction techniques adapted to be utilized together or separately in connection with such processes.

As is known, the most important molybdenum ores contain molybdenite (MoS_2) and/or oxidized molybdenum that is associated with iron. The more important deposits of ore, however, contain molybdenum largely as the sulfide, i.e., as MoS_2 . Although these molybdenum bearing ores seldom carry more than 1% or so of the mineral, methods having been developed whereby such ores are concentrated by flotation to produce a concentrate containing 90% or more of the molybdenum disulfide. In such an operation, however, that portion of the molybdenum found in the ore in an oxidized form is not floated but appears in the tailings. As far as is known, until recently no profitable commercial method of recovery of such oxidized forms has been known, and they have been simply discarded into flotation tailings ponds. Recently, however, a process has been discovered for concentrating these oxidized forms of molybdenum and converting them into compounds from which desired molybdenum values may more readily be recovered. This process is disclosed in copending application, Ser. No. 363,007, filed Apr. 27, 1964, now Patent No. 3,307,938, and assigned to the assignee of the present invention.

In this disclosed process the ore is first preconcentrated on the basis of the iron oxide with which the molybdenum values are associated, the result being the formation of a relatively high pulp density aqueous slurry. This slurry is then leached with a combination of sulfuric acid and gaseous sulfur dioxide, after which it is passed through a series of activated charcoal adsorption tanks where the molybdenum values are picked up by the activated charcoal. The loaded charcoal is then stripped with air, ammonia and water to form strip liquor containing ammonium molybdate. As disclosed, undesirable phosphorous values may be precipitated from the strip liquor as magnesium ammonium phosphate by adding magnesium sulfate to the solution. This strip liquor will contain ammonium molybdate, ammonium sulfate, free ammonia, dithionates, thiosulfates, and possibly traces of phosphorous and/or other impurities, depending on the content of the original ore.

It is therefore one of the principal objects of the present invention to provide an improved continuous process for economically extracting molybdenum values from the pregnant charcoal adsorption strip liquor of the process disclosed in said copending application.

Another object of this invention resides in the provision of an extremely selective continuous solvent extraction process for commercially recovering molybdenum values. A related object resides in the provision of such a process of the liquid ion exchange type utilizing an amine extractant.

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A further object concerns the provision of a continuous solvent extraction process for molybdenum wherein any tendency to form troublesome sludge or slimes is minimized. A related object concerns the provision of such a process wherein sludge and slime control is achieved by pH regulation.

Another object resides in the provision of a continuous commercial solvent extraction process wherein extraction is extremely selective for molybdenum, and more specifically molybdenum in the form of molybdenum blue, a complex acid colloid. A related object concerns the provision of such a process utilizing a tertiary amine extractant at a pH above its neutral point.

A further object resides in the provision of a combined precipitation and solvent extraction process wherein acidification of the mother liquor not only causes the precipitation of a substantial amount of the molybdenum values but also adjusts the liquor pH to an ideal value for a very selective solvent extraction process in which the tendency for slimes and the like to form is minimized.

Another object resides in the provision of a continuous process for commercially recovering molybdenum values from a solution of ammonium molybdate and ammonium sulfate. A related object concerns the provision of such a process in which separation is effected at relatively low concentrations of the molybdenum containing constituent of the feed.

Another object resides in the provision of a continuous evaporation-crystallization process for selectively recovering molybdenum values from a solution of ammonium molybdate and ammonium sulfate, wherein a portion of the solution is bled from the crystallizer and processed to remove the sulfur compounds therefrom prior to recycling back to the crystallizer, whereby the sulfur concentration in the crystallizer never reaches the saturation point. A related object concerns the provision of a novel process for treating said bleed liquor.

These and other objects of this invention will become apparent from consideration of this specification, the appended claims, and the accompanying drawing in which there is shown a flow sheet of a process embodying the principles of the present invention.

Generally speaking, in the process disclosed herein the input liquor is first processed through a continuous evaporator-crystallizer circuit to convert the ammonium molybdate to ammonium paramolybdate crystals, which are then filtered out and calcined to obtain the molybdc oxide final product. Approximately 85% of the molybdenum in the input liquor may be recovered in this manner. To prevent the build-up of an excessive sulfate concentration in the crystallizer, a portion of the mother liquor is bled from the crystallizer circuit and the remaining molybdenum values, approximately 15% of the original amount, are in this bleed. An acid is added to the bleed liquor to reduce its pH to approximately 5, thus causing 85% to 90% of the molybdenum to precipitate out as ammonium paramolybdate, which may then be separated by filtration and calcined along with the ammonium paramolybdate recovered in the crystallizer circuit. The unprecipitated molybdate therein is then reduced to molybdenum blue, a complex acid colloid, which is then very selectively extracted with a tertiary amine extractant operating at a pH greater than its neutral point. The molybdenum values are then stripped from the extractant with ammonia and water. The resulting ammonium molyb-

date is then reintroduced into the crystallizer, free of sulfates, and the molybdenum values therein recovered in the above manner.

The specific process which will now be described, embodying the principles of the present invention, is one which has been found through pilot plant studies and the like to be preferable for the commercial extraction of molybdenum values from the strip liquor resulting from the process disclosed in said copending application Ser. No. 363,007, for processing the molybdenum ore now being mined at Climax, Colorado. As will be appreciated, however, the details of the process disclosed herein may be varied in accordance with known criteria and phenomena for the extraction of molybdenum values from different input solutions. Furthermore, certain of the sub-processes disclosed herein, particularly the solvent extraction process, may be used independently of other parts of the overall process, as will be obvious to one skilled in the art and familiar with the principles of the present invention as taught by the disclosed embodiment thereof.

In the exemplary system disclosed herein the input feed is a filtrate containing primary ammonium molybdate and ammonium sulfate, and also smaller amounts of free ammonia, dithionates, thiosulfates, and possibly a trace of phosphorous. It is believed that dithionates and polythionates were formed in the previous leaching circuit, probably by the reaction between sulfur dioxide, sulfuric acid and pyrrhotite. These polythionates were then apparently absorbed by the charcoal along with the molybdenum. The dithionates were rejected by the charcoal and discarded with the tailings. During the subsequent ammonia strip of the charcoal the polythionates were probably broken down to thiosulfates and therefore accompany the molybdenum input to the present circuit. The pH of the solution is approximately 9.0 to 9.5 and it contains approximately 70 grams Mo per liter of solution, approximately 7 grams sulfur per liter of solution, and approximately 0.35 grams NH_3 per gram Mo.

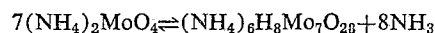
In order to drive off the NH_3 for recovery and to increase the concentration of ammonium molybdate, this input solution is first passed through a continuous evaporator. The evaporator is preferably operated at approximately 185°F ., using steam if desired, and at a vacuum of about 5–10 in. Hg absolute. The use of a vacuum not only increases the efficiency of the evaporation process but also serves to prevent the formation of molybdenum blue, a complex acid colloid, which would be detrimental to the subsequent crystallization step of the process. Substantially all of the ammonia is removed in the evaporator and the resultant concentrated liquor has a pH of approximately 7, approximately 100 grams Mo per liter of solution and 10 grams sulfur per liter of solution.

The liquor passes from the evaporator through a heat exchanger in which it is preheated to approximately the operating temperature of the subsequent crystallization operation.

It has been discovered that in a solution of this type, as the sulfur concentration increases the solubility of the molybdate drops off rapidly. Consequently, it has been found that by feeding this concentrated liquor into a continuously operating vacuum crystallizer, where it is further concentrated by evaporation, continuously removing from the crystallizer the resulting ammonium paramolybdate crystals which are formed, and continuously bleeding off a sufficient amount of mother liquor from the crystallizer circuit to prevent the sulfur concentration from reaching the saturation point and replacing it with a like amount of water or a solution containing little or no sulfate, it is possible to recover a substantial portion of the molybdenum in the mother liquor as ammonium paramolybdate crystals. Tests indicate that if the total sulfur concentration is allowed to increase by evaporation to approximately 103 grams per liter and then maintained at that level, the solubility of the molybdate will be ap-

proximately 100 grams Mo per liter. Thus, once this equilibrium has been reached if sufficient mother liquor is bled from the crystallizer to maintain the total sulfur concentration at about 103 grams per liter, approximately 85% of the input molybdate may be recovered by crystallization as ammonium paramolybdate, and this may be accomplished at relatively low molybdate concentrations, not much more than its concentration in the original feed liquor. This equilibrium condition in the crystallizer represents the practical limit of ammonia removal and conversion of normal ammonium molybdate to paramolybdate, by evaporation, without prohibitive contamination of the crystallizer product with ammonium sulfate, while yet utilizing the maximum salting-out effect of the sulfur on the ammonium paramolybdate.

In the crystallizer ammonium paramolybdate is precipitated when free ammonia is removed from solution and normal ammonium molybdate is converted to paramolybdate by the following general reaction:



Preferably the crystallizer is operated at $110^\circ\text{--}120^\circ\text{F}$. and at a vacuum of about 4 in. Hg absolute, the vacuum pump drawing out the NH_3 and evaporated water. An analysis of the mother liquor in the crystallizer shows that in addition to the 103 grams total sulfur per liter and 100 grams Mo per liter, it contains about 85 grams sulfur in sulfate form per liter (the difference between the two sulfur figures is believed to be due to the presence of thiosulfates), about 126 grams NH_3 per liter, has a pH of approximately 7.0–7.5, and has a Total Reducing Power, expressed as equivalent KMnO_4 per liter, of about 2.6. This is also the analysis of the mother liquor bleed. An analysis of the crystals formed, on a wet basis, is 49.5% Mo, 8.7% NH_3 and 0.3% total sulfur.

The chemistry of the molybdenum and sulfur compounds during evaporation has never been satisfactorily explained. It was observed that if evaporation is conducted at a boiling point of around 205°F ., the solution turns progressively darker blue color, indicating the reduction of some molybdenum to the molybdenum blue, whereas if evaporation is conducted under a vacuum and at a temperature of 131°F ., the solution does not have the blue color but is brown. It is known that there are sulfur compounds other than sulfate in the feed liquor and it has been assumed that these are primarily thiosulfates. Because of the analytical problems on such unknown solutions, the exact form of the sulfur compounds has not been determined. However, these sulfur compounds have a total reducing power (T.R.P.) which is determinable by digestion in a sulfuric acid solution of ammonium metavanadate and titration of the reduced vanadium with potassium permanganate. If desired or necessary, the total reducing power of the solution can be oxidized by blowing with air for a long enough period of time at 95°C . In addition, the solubility of the molybdenum and ammonium sulfate is complicated by the pressure of these reduced sulfur compounds which are capable of reducing molybdenum. In spite of these uncertainties, however, a vacuum crystallizer operated in the manner taught above has been found to give very satisfactory results.

There are several ways in which the bleed liquor can be handled. It may be returned to the crystallizer after the sulfate is removed, it may be discarded and an equivalent amount of water returned to the crystallizer, or a portion or all of the remaining molybdenum values may be extracted by any desired procedure outside the crystallizer and returned to the crystallizer while the residue containing the sulfate and other impurities but not the molybdate is discarded. One of the aspects of the present invention is the provision of a unique precipitation and solvent extraction process for accomplishing this latter course. Treating a small portion of the mother liquor from the crystallizer circuit to remove the residual molybdenum and discarding all the remaining liquor not only

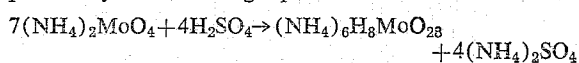
substantially improves the subsequent calcining operation by eliminating the need to volatilize large quantities of ammonium sulfate, but also provides a bleed from the crystallizer of ions such as the alkalis and fluorides so that they will not build up to saturation, with attendant corrosion effects or interference with crystal formation.

The mother liquor containing the ammonium paramolybdate crystals flows in the crystallizer circuit to a settler in which the crystals are separated from the mother liquor. At this point in the process the mother liquor bleed is taken from the flow. The settled crystals are then vacuum filtered and washed with about one replacement volume of water, the resultant filtrate (mother liquor plus wash water and less the crystals) being communicated back to the crystallizer so that unrecovered molybdenum values therein may be recovered and the equilibrium conditions in the crystallizer maintained. The ammonium paramolybdate crystals from the filter are transported to a calciner, in which they are rotated for approximately 30 minutes at a temperature which may range from about 1000 to 1070° F. The calcining operation converts the ammonium paramolybdate to molybdic oxide (MoO_3), driving off ammonia. Also, any fluorine present is driven off as ammonium fluoride, any sulfate as ammonium sulfate, dithionates as ammonium sulfite, and should it exist any free sulfur is burned off. The molybdic oxide output of the calciner is in powder form, and has been found to be of extremely high purity, higher than technical grade.

As mentioned briefly above, the mother liquor bleed is treated to extract the molybdenum values therefrom. This bleed liquor contains from 10% to 15% of the molybdenum in the feed liquor (i.e., 10-15 grams Mo per liter), is substantially saturated with ammonium sulfate, and is relatively concentrated with respect to other impurities such as the alkali elements, fluoride, and so on. There are several ways that this bleed liquor may be treated, such as acidification followed by adsorption on charcoal, fractional crystallization, or solvent extraction. On the basis of tests made it has been found that solvent extraction is a very satisfactory method to use to recover the molybdenum from the mother liquor bleed so that it can be returned to the crystallizer for further recovery processing. This technique permits the discarding of all of the ammonium sulfate and other impurities in the raffinate from the solvent extraction operation.

As will be discussed in greater detail below, it has been discovered that a pH value of from approximately 4.5 to 6.0, and preferably about 5, is ideal for the solvent extraction process, using the preferred extractant. Accordingly the mother liquor bleed is pumped into tanks where sufficient sulfuric acid is added incrementally to adjust the acidity thereof from a pH of 7.0-7.5 to a pH of approximately 5 and maintain it there. In acidifying the bleed liquor it was discovered that if the solution in the tanks is digested with agitation for about 4-5 hours, approximately 85% to 90% of the molybdenum values therein will precipitate out as ammonium paramolybdate. For example, the addition of 0.5 lb. of 100% sulfuric acid per pound Mo to the mother liquor bleed with a contact time of about four hours at a temperature of about 75°-120° F. (ambient temperature), gave the desired pH of about 5 and resulted in a recovery of approximately 89% of the molybdenum in the mother bleed liquor. The precipitation tanks may be operated continuously and at atmospheric pressure.

During the acidification and precipitation operation, additional ammonia is removed from the solution and from the ammonium molybdate. This reaction can be expressed by the following equation:



Although the acid concentration at a pH of 5 is not necessarily optimum for the precipitation of ammonium para-

molybdate, it has been found to be best for the subsequent solvent extraction step of the process.

The mol ratio of molybdenum to ammonia found in the crystals precipitated at a pH of 5 was determined to be 1.29. This is slightly higher than the ratio 1.17 in ammonium paramolybdate. However microscopic examination indicates that the crystals are predominantly ammonium paramolybdate. Some molybdic acid is undoubtedly associated with the crystals, judging from the tendency for the pH of the solution to rise during precipitation.

The ammonium paramolybdate precipitate is then filtered and washed, the solids (ammonium paramolybdate) being carried to the calciner to be calcined along with the paramolybdate crystals from the crystallizer into the molybdic oxide final product. The filtrate, which contains only about 10% to 15% of the molybdenum in the bleed liquor, is then carried to the solvent extraction circuit.

Very little, if any, molybdenum blue, a complex acid colloid, exists in the mother liquor as it comes from the crystallizer. However, there are thiosulfates in the solution which operate to reduce a significant amount (about two-thirds) of the molybdate to molybdenum blue during acidification to a pH of 5. Molybdenum in this latter form is most selectively extracted by the present solvent extraction process. The filtrate from the precipitate filter is therefore heated for about one hour to just below the boiling point to thereby accelerate the reduction process started in the precipitation tanks, whereby the remainder of the molybdate in the bleed liquor is reduced to molybdenum blue. It is believed that this reduction process results from a decomposition of the thiosulfates into SO_2 , an effective reducing agent.

The filtrate plus wash water is then further diluted with water so that the final volume, prior to solvent extraction, is equal to about twice the volume of the original mother liquor. This serves to avoid post precipitation of salts which may now be almost at the saturation point and further crystallization, and facilitates the ease of handling the solution.

Concerning the solvent extraction process generally, the pH 5 feed is first passed through a series of counter-current mixer-settlers in a direction countercurrent to the flow of the organic solvent. The molybdenum blue is extracted by the extractant in the organic solvent in a highly selected manner and the pregnant solvent is then separated from the remaining portion of the mother feed liquor, or raffinate, which is then carried to tailings. The pregnant organic solvent then passes through a pair of strip settlers in series concurrently with a stripping solution of ammonia and water which strips the molybdenum values from the extractant and forms ammonium molybdate. The stripped organic then passes through a clean-up settler in which it is contacted with sodium carbonate and regenerated. The regenerated and now barren organic is then carried, along with any new organic which may be necessary for make-up, back to the last mixer-settler of the series, from which it flows countercurrently with respect to the mother liquor to complete the cycle. Since there is a pH change which tends to take place during the solvent extraction operation, sulfuric acid is added in sufficient amount to the barren organic just before it enters the last mixer-settler to insure that a stable pH in the desired range is maintained in all of the mixer-settlers. The acid is also needed because the solvent which is returning from the stripping circuit could be in an alkaline state and therefore would require acidification to prevent an increase of pH level in the final stages of the solvent extraction process. The equipment used and the manner in which the various materials are physically handled are conventional, except as may be described herein.

Through experimentation it has been discovered that a very satisfactory recovery of molybdenum blue may be effected using amines, and particularly tertiary amines,

as the extractant material. One such tertiary amine which is preferred is tritridecyl amine, manufactured by Archer Daniels Midland Company and sold under the trademark Adogen 383. This is a highly branched C₁₃ amine and is a derivative of tridecyl alcohol being produced by the oxoalcohol process. Another suitable amine is Adogen 368, a symmetrical trialkyl tertiary amine, manufactured by Archer Daniels Midland Company and having the structural formula:



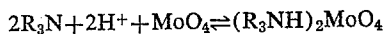
where R=C₁₀H₂₁.

A further tertiary amine found to be suitable is Alamine 304, a trilauryl amine manufactured by General Mills and having the structural formula:



where R=C₁₂H₂₃.

The use of amines for extraction of anions from a solution is generally applicable only for acidic solutions at a pH below the neutral point of the particular amine being used. The reaction involved can be represented by the following reaction, using the molybdate anion as an example:



Adogen 383 has a neutral point at a pH of 4.0, and both Adogen 368 and Alamine 304 have a neutral point at a pH of 4.5. Above this pH the reaction will ordinarily go to the left and no extraction of anionic species in the solution will take place. This has been demonstrated to be the case when molybdate and other metal anions such as vanadate, chromate or tungstate are to be extracted. However, it has been discovered that the extraction of molybdenum blue is unique in that the reaction unexpectedly does not go to the left until the pH reaches about 6. Consequently there is a pH range of about 4.0-6.0 where extraction is extremely selective for molybdenum.

Although molybdenum blue will extract very well at pH levels as low as 1, it has been discovered that at these pH levels precipitates are formed which tend to form stable emulsions in the solvent system. The exact composition of these precipitates is not known, however they contain a very large percentage of molybdenum and in all probability are a molybdic acid polymer or a hetero poly molybdate. For this particular liquor the pH level below which they become troublesome is about 4, although this level will vary depending upon the percentage of the molybdenum in the feed liquor which is in the molybdenum blue oxidation state.

Similar results may be obtained with other commercially available extractants, including secondary amines as well as other tertiary amines. Generally speaking, the specific properties which are sought in an extractant in the present process are as follows:

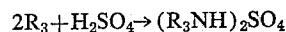
- (a) high molybdenum extraction coefficient;
- (b) insolubility in water and high solubility in organic diluents;
- (c) freedom from emulsion formation;
- (d) low vapor pressure;
- (e) high flash point;
- (f) freedom from third phase formation;
- (g) low toxicity;
- (h) low cost;
- (i) commercial availability;
- (j) chemical and physical stability.

Other such amines which will give similar results are as follows:

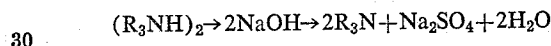
Trade Name	Supplier	Chemical Structure
Adogen 363.....	Archer Daniels Midland.	Trilaurylamine.
Adogen 364.....	do.	Tri C8-C10 (mixture of trioctyl, trinonyl and tridecyl amines).
Adogen 381.....	do.	Trisooctyl amine.
TIOA.....	Union Carbide.....	Do.
Alamine 336.....	General Mills.....	Tricaprylyl amine.
Amberlite LA-1.....	Rohm and Haas.....	Mixture of branched unsaturated secondary amines.

- 15 These extractants are most preferentially selective for molybdenum blue in the pH range just above their neutral point, the same as in the case of Adogen 383, Adogen 368 and Alamine 304. The neutral point is the pH at which the amine is all present as the free amine
- 20 R₃N) without any attached anions. It can be determined by conversion of the amine to the acid salt, and titration with a base using a pH meter to detect the end point by standard maximum deflection methods. These reactions are as follows:

- 25 (a) Conversion to acid salt



- (b) Titration



- 30 Quaternary amines are not particularly suitable in this circuit as described since they are best for extracting molybdate as well as molybdenum blue from neutral and ammoniacal solutions, and consequently could not be
- 35 stripped with ammonia.

- Although it has been found in some circumstances that the extraction coefficient for Alamine 304 (trilauryl amine) is not as high as the extraction coefficient for Adogen 368 (trialkyl amine) in the disclosed system, it is difficult to say which of these two extractants is best for a full scale commercial operation because the differences are so small, both of them working very satisfactorily. Adogen 383 (tritridecyl amine), however, is preferred because it has better phase separation characteristics, is less prone to form insoluble molybdenum sludges at lower pH levels and has a higher capacity for molybdenum.

- The solvent actually used in the process contains three primary constituents, an extractant, a diluent or organic carrier, and a coupling agent or modifier. The exact function of each of these constituents in the extraction process is not fully understood, but some general guide lines can be offered. The extractant is the active organic ingredient which forms a complex compound with the element which it is desired to extract from the aqueous solution, namely molybdenum here. This complex organic salt is soluble in the diluent, or organic carrier. The function of the carrier is therefore to serve as a solvent for both the organic extractant and the salt formed by the reaction between the organic extractant and the extracted element. The modifier serves a number of functions. The more important of these are to decrease emulsion formation, to improve the solubility of the organic materials in the diluent, and in many cases to act as a synergist and enhance the extraction coefficient.

- It has been found that very satisfactory results may be obtained with a solvent consisting essentially of 80% to 90% by volume of Solvesso 150 as the diluent, with the balance consisting essentially of substantially equal parts of Adogen 383 as the extractant and tributyl phosphate or isodecanol as the modifier. It is desirable to operate with as low a concentration of the active ingredient in the diluent as possible because this reduces the cost of any losses which may occur. Also lower concentrations usually have less emulsifying tendency.

Tri-butyl phosphate is preferred as the modifier in the present amine system because it is commercially available, relatively inexpensive, and most importantly because it works in improving the phase separation characteristics and general operability of the solvent system. Heavy alcohols, such as isodecanol, and other substances such as other neutral alkyl phosphate esters, including di-
 5 amyl phosphenate, are also suitable modifiers. The specific characteristics and properties sought are determined primarily on an empirical basis to enhance the extraction coefficient through synergism, and to improve the viscosity, phase separation and solubility characteristics of the solvent system.

The diluent which has been chosen, namely Solvesso 150, is an aromatic petroleum fraction of Humble Oil Company having the following specifications:

Total aromatics, percent	97.3
Flash point, tag closed cap, ° F.	151
Vapor pressure @ 100° F., p.s.i.a.	0.1
Initial boiling point, ° F.	364
Final boiling point, ° F.	416
Specific gravity 60/60° F.	0.8916
Pounds per gallon 60/60° F.	7.424
API gravity 60/60° F.	27.2
Viscosity centipoises @ 25° C.	1.177
Surface tension, dynes/cm., 25° C.	29.6

An aromatic solvent is preferred for this system rather than the normally used kerosene diluent because of superior phase separation characteristics and freedom from third phase formation. It is believed that many of the amines when used in a kerosene diluent are present as colloidal micelles rather than as true solution. In aromatic solvents, however, it is believed that the amines are a true solution, and as such their basicity and the solubility of the organic metal salt is much increased.

It has been discovered that the operating range for the solvent phase to aqueous phase ratio is very broad and that the preferred range varies substantially for different materials in the following way. If there are any emulsion forming solids present, the content of the solvent in the discharge raffinate is very materially lowered if the organic to aqueous phase ratio is kept quite high. This has the effect of making the organic the continuous phase in the mixing and the subsequent separation processes, and the quantity of entrained organic material in the aqueous is substantially reduced. On the other hand, if it is desired to have the solvent be as clear as possible, and clarity of the raffinate is not the determining factor, then it might be desirable to operate with the aqueous phase as the dominant one. In the present process it is preferable that the solvent phase be the continuous phase and that a phase ratio of about 1.5 to 3.0 to 1 (organic to aqueous) be used. This provides a stable operating system with a relatively small amount of solvent loss.

The feed to the solvent extraction circuit for the present process is at a pH of about 5 and contains about 7 grams Mo per liter of solution. Extraction is accomplished in three stages of countercurrent mixer-settlers using sufficient organic solvent to provide an organic phase to aqueous phase ratio of about 3. The mixer-settlers are operated at approximately 104° F. and a solvent loading of two grams Mo has been obtained. Strip is accomplished in two stages and sodium carbonate scrubbing in one stage. It has been found that approximately 0.4 lb. 100% H₂SO₄ per lb. Mo in the solvent extraction feed is sufficient when added to the regenerated barren organic to maintain the desired pH level, and that 0.4 lb. sodium carbonate per lb. Mo in the solvent extraction feed is sufficient to regenerate the organic. Static phase separation tests have shown that settler areas of approximately one foot per gallon per minute of combined aqueous and organic is adequate for settler sizing at an organic to aqueous ratio of 3:1.

The stripping circuit is a closed loop in which the strip liquor continually recycles co-currently with the pregnant

organic through the strip settlers, a portion thereof being continually bled from the circuit and passed through an activated carbon filter to remove any remaining traces of organic, which would be harmful to the subsequent crystallization operation. From the activated carbon filter the bleed or product liquor, which consists essentially of ammonium molybdate, is pumped back to the crystallizer circuit for recycling to recover the molybdenum values therein. The amount of product liquor pumped back to the crystallizer circuit is substantially the same in volume as the bleed liquor removed therefrom so that equilibrium will be maintained in the crystallizer circuit. A recycling type strip circuit is preferred because of the high ratio of solvent to aqueous. If the aqueous strip were not recycled, the ratio of solvent to aqueous in the mixers would be approximately 50:1, and this would result in inadequate contact.

Stripping is accomplished by continuously bubbling ammonia into one of the strip-settlers in the stripping circuit in an amount sufficient to insure that there is always an excess of free ammonia in the recycling strip solution. This ammonia reacts with the molybdenum values in the organic extractant to strip them therefrom and form ammonium molybdate. Since the operation of the extraction circuit at a pH of 5 utilizes amine extractants in the free base form no ammonia is consumed in reaction with an amine sulfate or bisulfate, which would occur if extraction was carried on at a lower pH. Also, since the ammonia associated with the ammonium molybdate, as well as any excess ammonia in the solution, is returned to the crystallizer and recovered, the net consumption is only that which reacts with the sulfate in the strip solution. It has been found that NH₃ consumption in the stripping circuit is only approximately 0.04 lb. NH₃ per pound Mo.

Just prior to the product liquor bleed from the stripping circuit the strip liquor is oxidized by heating it to approximately 149° F. and passing air through it for a residence time of about three hours to convert a major portion of the molybdenum blue which may be in the liquor to the molybdate form. This prevents the precipitation of a black sludge in the settlers.

Solvent loading is normally about two grams Mo per liter. Consequently, since it is preferred that the molybdenum concentration in the product liquor stream returning to the crystallizer be at approximately the same concentration as the mother liquor bleed, i.e., about 100 grams Mo per liter, the bleed stream from the strip liquor circuit will be approximately $\frac{2}{100}$ or 2% of the solvent flow. The strip circuit is supplied with water in an amount equal to the amount of the product liquor bleed to maintain equilibrium therein. The strip solution contains approximately 85 to 100 grams Mo per liter of solution and the total recovery of molybdenum from the solvent extraction feed has been found to be about 93%. The recovery of molybdic oxide for the entire circuit, including crystallization, precipitation and solvent extraction, is over 90%.

The mother liquor bleed from the crystallizer circuit may be treated by an alternative process which is substantially the same as that described above except that the solvent extraction system is operated at a pH of about 3.5 using Adogen 383 (tridecyl amine). This pH is below the neutral point of this amine and consequently the amine extracts both molybdenum blue and molybdate. In this alternate process, since the pH of the mother liquor bleed is brought to a lower level there is a more complete precipitation of ammonium paramolybdate. Also since the amine extracts molybdate as well as molybdenum blue, the heating step prior to solvent extraction may be eliminated because there is no need to effect a reduction of the molybdenum to molybdenum blue. On the other hand, this alternative process requires the use of a substantially increased amount of acid for adjustment of the pH to the lower level, as well as a substantially increased amount of ammonia for stripping the molybdenum values from the solvent.

Whether or not this alternative process is preferable to that disclosed above in any given commercial operation will of course depend upon a weighing of these factors.

As is evident, the present invention resides in the provision of novel recovery processes. It is not limited to the use of any specific type of apparatus or equipment. As noted previously, the various equipment used in practicing the present process is conventional in construction and the physical manipulation of the various feeds is conventional except as otherwise noted. Furthermore, in the examples set forth the ranges, amount, and so on are those which are preferable for extraction of molybdenum value from feeds of the type set forth. Feeds differing somewhat from those described herein may obviously be also treated by the present process, the only changes necessary being those which will be readily apparent to those skilled in the art in light of the teachings of the present disclosure.

Thus, there is disclosed in the above description and in the drawing two exemplary processes embodying the principles of the present invention which fully and effectively accomplish the objects thereof. However, it will be apparent that variations in the details set forth may be indulged in without departing from the sphere of the invention herein described or the scope of the appended claims.

What is claimed is:

1. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the concentration of other substances which may be therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; extracting molybdenum from the remaining bleed liquor with an organic extractant; and stripping the molybdenum values from the pregnant organic extractant.

2. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; extracting the molybdenum from the remaining bleed liquor with an organic extractant; stripping the molybdenum values from the pregnant organic extractant with ammonia and water thereby forming ammonium molybdate; and recycling the strip liquor back to the crystallizer.

3. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration there-

in from reaching the saturation point and precipitating; filtering the ammonium paramolybdate crystals from the mother liquor and returning the filtrate to the crystallizer; heating the filtered ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; filtering the bleed liquor precipitate and heating the resulting paramolybdate solids to drive off ammonia and form a molybdic oxide final product; extracting the molybdenum from the remaining bleed liquor with an organic extractant; stripping the molybdenum values from the pregnant organic extractant with ammonia and water thereby forming ammonium molybdate; and recycling the strip liquor back to the crystallizer.

4. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; extracting the molybdenum from the remaining bleed liquor with an organic extractant; stripping the molybdenum values from the pregnant organic extractant with ammonia and water thereby forming ammonium molybdate; oxidizing the resultant strip liquor to decrease the amount of any molybdenum blue therein by converting it to molybdate; and recycling the oxidized strip liquor back to the crystallizer.

5. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to a pH of from about 4.0 to 6.0 with sulfuric acid to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; heating the remaining bleed liquor in the presence of a reducing agent to convert the remaining molybdenum values to molybdenum blue, a complex acid colloid; extracting the molybdenum blue with an amine extractant; stripping the molybdenum values from the pregnant amine extractant with ammonia and water thereby forming ammonium molybdate; and recycling the strip liquor back to the crystallizer.

6. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; filtering the ammonium paramolybdate crystals from the mother liquor and returning the filtrate to the crystallizer; heating the filtered ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide

final product; acidifying the mother liquor bleed with sulfuric acid to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; filtering the bleed liquor precipitate and heating the resulting paramolybdate solids to drive off ammonia and form a molybdic oxide final product; extracting the molybdenum from the remaining bleed liquor with an organic extractant; stripping the molybdenum values from the pregnant organic extractant with ammonia and water thereby forming ammonium molybdate; oxidizing the resultant strip liquor to decrease the amount of any molybdenum blue therein by converting it to molybdate; and recycling the oxidized strip liquor back to the crystallizer.

7. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; filtering the ammonium paramolybdate crystals from the mother liquor and returning the filtrate to the crystallizer; heating the filtered ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to a pH of from 4.0 to 6.0 with sulfuric acid to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; filtering the bleed liquor precipitate and heating the resulting paramolybdate solids to drive off ammonia and form a molybdic oxide final product; heating the resultant bleed liquor filtrate in the presence of a reducing agent to convert the remaining molybdenum values to molybdenum blue, a complex acid colloid; extracting the molybdenum blue with an amine extractant; stripping the molybdenum values from the pregnant amine extractant with ammonia and water thereby forming ammonium molybdate; oxidizing the resultant strip liquor to decrease the amount of molybdenum blue therein by converting it to molybdate; and recycling the oxidized strip liquor back to the crystallizer.

8. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to a pH of approximately 5 to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; heating the remaining bleed liquor in the presence of a reducing agent to convert the remaining molybdenum values to molybdenum blue, a complex acid colloid; extracting the molybdenum blue with a tertiary amine extractant; stripping the molybdenum values from the pregnant extractant with ammonia and water thereby forming ammonium molybdate; and recycling the strip liquor back to the crystallizer.

9. A process as claimed in claim 8, wherein said tertiary amine is a tritridecyl amine.

10. A process as claimed in claim 8, wherein said tertiary amine is a symmetrical trialkyl amine.

11. A process as claimed in claim 8, wherein said tertiary amine is a trilauryl amine.

12. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating

the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; bleeding off a sufficient portion of the mother liquor from the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating; heating the ammonium paramolybdate crystals to drive away ammonia and thereby form a molybdic oxide final product; acidifying the mother liquor bleed to cause a precipitation of further molybdenum as ammonium paramolybdate crystals; heating the resulting paramolybdate crystals to drive off ammonia and form a molybdic oxide final product; heating the remaining bleed liquor in the presence of a reducing agent to convert the remaining molybdenum values to molybdenum blue, a complex acid colloid; extracting the molybdenum blue with an organic extractant selected from the group consisting of secondary and tertiary amines and mixtures thereof at a pH greater than the neutral point of the amine; stripping the molybdenum values from the pregnant extractant with ammonia and water thereby forming ammonium molybdate; and recycling the strip liquor back to the crystallizer.

13. A process as claimed in claim 12, wherein said organic extractant is a tritridecyl amine.

14. A process for extracting molybdenum values from an aqueous solution containing molybdenum blue comprising the steps of contacting the solution with an organic solvent containing an amine extractant while maintaining the pH of the solution during extraction at a level greater than the neutral point of said amine extractant, and thereafter stripping the molybdenum values from the amine extractant.

15. A process as claimed in claim 14, wherein said amine extractant is selected from the group consisting of secondary and tertiary amines and mixtures thereof.

16. A process as claimed in claim 14, wherein said amine extractant is a tritridecyl amine.

17. A process as claimed in claim 14, wherein said solution is maintained at a pH ranging from 4.0 to 6.0.

18. A process as claimed in claim 14, wherein the solvent phase to aqueous phase ratio is maintained between about 1.5 to 3.0.

19. A process for extracting molybdenum values from an aqueous solution containing molybdenum blue comprising the steps of contacting the solution with an organic solvent containing a tertiary amine as an extractant, a modifier selected from the group consisting of isodecanol and tributyl phosphate and mixtures thereof, and an aromatic petroleum solvent as a diluent, while maintaining the pH of the solution during extraction at a level greater than the neutral point of said amine, and thereafter stripping the molybdenum values from the amine extractant.

20. A process for extracting molybdenum values from an aqueous feed solution which comprises the steps of providing an organic solvent containing an amine extractant, acidifying said feed solution containing the molybdenum values to a pH greater than the neutral point of said amine extractant, reducing the molybdenum values in said feed solution to molybdenum blue, contacting said feed solution with said organic solvent and extracting molybdenum blue from said feed solution with said amine extractant while maintaining the pH of said feed solution during extraction at a level greater than the neutral point of said amine extractant, separating said feed solution from said organic solvent and thereafter stripping the molybdenum values from said organic solvent.

21. A process as claimed in claim 20, wherein said amine extractant is selected from the group consisting of secondary and tertiary amines and mixtures thereof.

22. A process as claimed in claim 20, wherein said amine extractant is a tritridecyl amine.

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23. A process as claimed in claim 20, wherein said amine extractant is a trialkyl tertiary amine.

24. A process as claimed in claim 20, wherein said amine extractant is a trilauryl tertiary amine.

25. A continuous process for recovering molybdenum values from an aqueous solution containing ammonium molybdate and ammonium sulfate, comprising: heating the solution under a vacuum in a continuous crystallizer to drive off water and ammonia, thereby precipitating molybdenum as ammonium paramolybdate crystals; continuously removing the crystals from the mother liquor in the crystallizer; continuously bleeding off a sufficient portion of the mother liquor in the crystallizer to prevent the sulfate concentration therein from reaching the saturation point and precipitating, and maintaining it at a point just below saturation; treating the bleed liquor to remove the sulfate values therein; and continuously adding to the crystallizer makeup free from sulfate values in an amount sufficient to maintain flow equilibrium therein.

26. A process as claimed in claim 25, wherein said makeup comprises said bleed liquor after the sulfate values have been removed therefrom.

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27. A process as claimed in claim 26, wherein the molybdenum concentration in said makeup is substantially the same as in the mother liquor in the crystallizer.

28. A process as claimed in claim 25, wherein said removal of ammonium paramolybdate crystals from the mother liquor in the crystallizer is accomplished by filtration, and returning the resultant filtrate to the crystallizer.

29. A process as claimed in claim 28, wherein said makeup comprises said bleed liquor after the sulfate values have been removed therefrom.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,357,821

December 12, 1967

Angus V. Henrickson

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 46, after "pregnant" insert -- organic --; column 8, line 26, for "2R₃" read -- 2R₃N --; column 9, line 1, for "Tri-butyl" read -- Tri butyl --; column 11, line 11, for "amount" read -- amounts --; line 13, for "value" read -- values --.

Signed and sealed this 4th day of March 1969.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents