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METHOD OF PREPARATION OF METAL SALTS

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The present invention relates generally to metal corrosion and the preparation of metal compounds and is more particularly concerned with a novel and very economical and useful method of preparing metal derivatives such as salts and sulfides, and with a method of separating the metal values of alloys rapidly, economically and very sharply.

The chemical art has long been concerned with the problem of metal corrosion and substantial progress has been made in the application of certain very corrosion-resistant metals, such as nickel, and in the development and application of special corrosion-resistant alloys like Monel metal, Chromel and brass. Efforts made in the opposite direction, i. e. to devise practical means and methods of overcoming resistance of such metals and alloys to corrosion in order to produce compounds thereof, have, however, not heretofore met with any noteworthy success, to the best of my knowledge. In the case of nickel, the production of nickel salts directly from metallic nickel has never heretofore been a fully satisfactory commercial operation primarily because of the inconsistency with which nickel tends to dissolve and the excessive cost in time involved in such production due to nickel passivity. Thus, in accordance with one particular procedure which has been attempted in various forms, many times nickel is contacted with concentrated sulphuric acid (50% by weight) and at first begins to corrode at a reasonably good rate producing nickel sulphate. However, before the reaction proceeds to the point where substantial corrosion is effected, the reaction slows down practically to a standstill due to the hydrogen over-voltage developed on the surface of the nickel. The resulting passivating effect on the nickel body is virtually complete and no matter how much the acid concentration is increased, the corrosion rate is not materially affected. No known means, chemical or physical, has hitherto been consistently capable of relieving this condition although virtually everything has been tried. Thus, efforts to operate under high temperature or high pressure circumstances have failed insofar as their object has been to relieve the passivity of the nickel.

Similar problems and difficulties present themselves when an attempt is made to produce salts of nickel other than the sulphate or the chloride or to produce salts of metals other than nickel, starting with the metal in its elemental form. Nickel, for instance, is corrodable in accordance with the best prior art practices using, for example, acetic acid, at only a very slow and completely unsatisfactory rate, regardless of the temperature, pressure, acid concentration or other physical or physical-chemical or chemical circumstances. Other metals classed with nickel and copper as corrosion resistant because of these characteristics include aluminum, cobalt, zinc, cadmium, chromium, lead, antimony, tin, iron and molybdenum. It will, therefore, be understood that while a given metal may present no substantial corrosion resistance to certain acids, it may be quite resistant to attack by other acids, and that the present invention process has

special utility in respect to this latter situation, particularly where it is desired to produce directly, rapidly, economically and commercially a salt of such metal made from a weaker acid.

In the case of Monel metal, again, the production of nickel and copper compounds therefrom has always been a slow and expensive operation and of no commercial significance because of this and because of the added difficulty of making a good separation of the compounds obtained. One prior art procedure, which to the best of my knowledge has never enjoyed commercial success to any extent, although patented by a large chemical manufacturing concern, involves subjecting a mixture of finely divided Monel metal and water to the action of sulphur dioxide under elevated temperature and pressure conditions. Under high pressures, such as 65 to 70 pounds per square inch gauge, appreciable corrosion of the alloy and production of nickel sulphate and copper sulphate results in accordance with this method. Nevertheless, the rate of corrosion obtained is not sufficiently rapid to make the process attractive commercially, particularly since a special nickel sulphate-copper sulphate separation operation must be carried out after the corrosion step is finished, and this operation involves conversion of the copper sulphate to copper sulphide and a subsequent slow filtering step. Moreover, the use of pressure entails a substantial initial expense for special equipment.

According to another Monel conversion process, which incidentally has also been patented by the company referred to above and has not been practiced commercially, the alloy is subjected to the action of dilute sulphuric acid under conditions of an abnormal concentration or partial pressure of oxygen and an elevated temperature such as about 90° to 100° C. If the air used is not under pressure, free oxygen must be added to the air to produce the stated results. In any event, even though free oxygen and super-atmospheric pressure are employed together, the rate of corrosion of the alloy is so slow that this method is impracticable particularly in view of the substantial additional time and expense involved in separating the sulfate reaction product of nickel and copper, as indicated above. The additional expense which the use of pressure and/or oxygen in this manner would entail, makes the process even less feasible economically.

In accordance with my present invention, which is based upon my surprising discoveries subsequently to be described, it is possible, for the first time to my knowledge, to increase materially the rate of corrosion of metals and alloys such as those mentioned above, and at the same time to produce derivatives of these metals and alloys which may be rapidly and easily separated. Thus, for instance, nickel and copper in the form of Monel metal or as individual elements can be charged into a reaction vessel and converted in accordance with this invention, the nickel salt resulting being soluble and going into solution in the reaction mixture, while the copper derivative is produced as a solid which accumulates on the bottom of the vessel as an easily filterable sludge-like material. This is a very practical and economical method and at the present time is being applied commercially successfully to nickel and to Monel metal in relatively small scale operations but at a high margin of profit, compared to any and all prior art Monel conversion processes. It is also possible, according to my invention, to prepare rapidly and economically metal compounds from other metal values. For example, nickel sulphate can be made from nickel sulphide-copper sulphide by subjecting the mixed sulphides to the action of sulphur dioxide in an aqueous sulphuric acid solution.

Failure of the prior art in this connection and the success of this present process is attributable entirely to my aforesaid discoveries a basic one of which, briefly stated,

is that sulphur dioxide under special circumstances will function very effectively and rapidly to convert normally very corrosion-resistant metals and metal alloys into metal compounds, such as salts and sulphides. The reactions involved take place almost instantaneously where conditions are proper and accordingly the process may be carried out in liquid media which are practically at their boiling point temperatures and in which the concentration of sulphur dioxide at any given time can thus not possibly be substantial. I have further discovered that where a metal stands above hydrogen in the electromotive force series, the use of sulphur dioxide in a particular manner will result in the rapid corrosion of the metal and the production of the salt of the metal of the acid present in the reaction mixture. Still further, I have found that where the metal involved stands below hydrogen in the said series, the corrosion of the metal carries forward at a similarly rapid rate with the result that the sulphide of the metal is produced. Generally, therefore, the corrosion in accordance with this process of the metal above hydrogen results in production of a salt solution of that metal, while the corrosion of the metal below hydrogen results in the production of the sulphide of that metal which normally will be insoluble in the reaction solution and will accumulate as a sludge-like deposit on the bottom of the reaction vessel. I have additionally discovered that metals behave according to the foregoing rules when they are delivered into the reaction mixtures of this invention in alloy form. Thus, where an alloy contains or consists of a metal above hydrogen and a metal below hydrogen in the said series, the use of sulphur dioxide in a particular manner will result in the rapid production of a salt of the higher standing metal, and in the simultaneous production at the same rate of the sulphide of the metal below hydrogen. Further, I have found that where an alloy contains or consists of two metals, both of which are above hydrogen, the salt of each of the metals will be produced. On the other hand, where the alloy contains or consists of two metals, both of which stand below hydrogen in said series, the sulphides of these metals will be produced.

In producing the foregoing results in the process of my invention, sulphur dioxide behaves in a novel and hitherto unknown manner. Thus, instead of being oxidized with resulting production of sulphate radical, the sulphur dioxide is reduced through the reactions of this process so that elemental sulphur is formed and precipitated from the liquid phase of the reaction mixture of this sulphur dioxide sulphur is converted into a sulphide compound. Elemental sulphur results as an end product where there is no metal below hydrogen available in the reaction mixture for sulphide production.

Very generally, the method of this invention comprises the step of treating a metal with sulphur dioxide in an aqueous solution containing more than about 0.5% by weight of a strong acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrochloric acid, hydrofluoric acid, nitric acid and phosphoric acid.

Preferably, the metal is in comminuted form in order that the surface thereof available for corrosion will be at a maximum for greatest production and efficiency. The temperature of the mixture is, for the same reason and purpose, maintained relatively high throughout the process even though appreciable corrosion of the metal may be realized at room temperature, i. e. about 65° to 70° F. Temperatures in the range between about 80° C. to about 100° C. or higher up to the boiling point temperature of a given reaction mixture under atmospheric pressure, will however, generally be found to produce the best results from the standpoint, at least, of corrosion reaction rates. Air can be, to this same general purpose, bubbled into the solution while the process is going on, since the agitating effect thereby obtained in the solution assures clean metal surfaces for reaction and substantial uniformity of acid concentration throughout the solution. In general, any gas or mixture of gases not having a deleterious effect on the process may be used to accomplish this agitation to advantage, but air will normally be preferred for reasons of economy and also because of its free oxygen content to which, I believe, certain advantages in the preferred practice of this invention subsequently to be described, are attributable.

Pressure is not necessary to the practical and commercial operation of this process and, in fact, has relatively little effect upon the course of the corrosion reactions, even though it may enable the application of somewhat higher temperatures to the reaction mixture, and super-atmospheric pressure is accordingly not preferred in the best practice of the invention. Sub-atmospheric pressures result in depression of boiling point temperatures and to this extent, at least, are not preferred for use in the present process.

The acids suitable for use in the process include those which are substantially completely soluble in water (without substantial decomposition), i. e. to an extent greater than about 80% on the basis of the volume of water employed. These acids also have other properties in common, namely a relatively high ionization potential and substantial stability against the decomposing effects of heat up to approximately the boiling point temperatures of the present reaction mixtures under substantially atmospheric pressure. Thus, these acids are quite effective in dilute aqueous solution and exert their effects noticeably even in relatively very small concentrations, such as down to about 0.5%. I have found, however, that the foregoing novel results and advantages of this invention cannot be obtained where the concentration of acid in the reaction mixture is less than about 0.5% at the beginning of the reaction period or for the greater proportion of that period. This is due to the fact that the unique sulphur dioxide reaction of this invention apparently does not take place when the concentration of acid is below that minimum value.

The acids specified above may be used singly or in any desired combination with the understanding however, that certain of them will be incompatable such as nitric acid and formic acid or acetic acid, and that it would not ordinarily serve any useful purpose to combine such acids in a single medium. The acid concentration, whether one or more acids are used, should not be maintained any lower than the minimum stated above because the process and the metal corrosion reactions involved therein will then proceed too slowly for practical purposes. It will be understood, therefore, that the acid concentration of a solution for use in this process should initially be substantially in excess of 0.5%, but that it may be approximately 0.5% and be maintained at substantially that value. In the absence of detectable (by standard sensitive acid determination techniques) amounts of acid in the solutions employed in this process, the reactions and results of this invention are apparently not affected or obtained. In practice, I prefer to maintain the acid concentration above about 2% by weight throughout the major portion of the reaction (corrosion) period, and I have found that better results are to be obtained where this concentration is still higher, as above about 5% to 10%. As long as there is some water present, the process may be carried out with the foregoing results and consequently no maximum limit need be fixed on the concentration of the acid in the solution. As a practical matter, however, a concentration of 50% to 60% of sulphuric acid will be found a reasonable maximum for either "initial" or "maintained" concentrations inasmuch as results obtained above this level will not ordinarily be sufficiently improved to justify the greater expense involved in the use of excessive amounts of acid.

As used herein, the term "corrosion" means and refers to chemical, rather than physical, conversion of a substance. Thus, in accordance with my usage of the term, "corrosion" defines the action involved in making

a metal compound, such as a salt or a sulphide, from a metal in elemental form.

From the foregoing, it will be understood that an alloy of two or more metals may be used, rather than a single metal, in which case a plurality of metal compounds will be produced. These compounds will be salts or sulphides of the metals used, depending upon the position of these metals with respect to hydrogen in the electromotive force series. The rule stated above governing this matter of metal products is applicable fully regardless of what metals or combinations of alloys thereof are employed as starting materials, and regardless of which of the specified acids or combinations thereof are employed in the reaction mixture. Thus, the metals in an alloy of four or five constituents, which has hitherto withstood all efforts to separate and recover economically the values therein can be treated successfully in accordance with this invention and at the outset of my process a separation between the metals above and below hydrogen will be obtained as the corrosion reactions go on.

The expressions "above hydrogen in the electromotive force series" and "below hydrogen in the electromotive force series," are employed herein and in the appended claims in accordance with general usage and understanding in the art. Thus, the first expression identifies a metal which is electronegative with respect to hydrogen, such as nickel or chromium, and the second expression identifies a metal which is electropositive with respect to hydrogen, or in other words, a metal such as mercury or copper.

There is, among those skilled in the art, some doubt and disagreement as to the proper positions of some elements in the electromotive force series. For the purpose of this invention and specification, however, the table set out on page 1380 of Handbook of Chemistry and Physics (28th edition) by Charles D. Hodgman (published by Chemical Rubber Publishing Co.), may be consulted in determining the relative position of a given metal element with respect to hydrogen in the said series.

The metals and alloys which are especially suited for use in this process are those relatively corrosion resistant metals and alloys, such as aluminum, nickel, cobalt, zinc, cadmium, chromium, lead, antimony, tin, iron, copper, molybdenum, nickel alloys like Monel metal and Chromel, copper alloys including copper-mercury amalgams, cobalt-copper alloys, cobalt-arsenic alloys, brasses and bronzes. The method of this invention, however, is not limited to use with or on these particular materials, but may be applied more generally to mixtures of two or more of these metals and alloys, as well as to other less common corrosion resistant metals and alloys to produce metal or alloy corrosion compounds of metals including sulphides and salts. Silver and silver alloys are representative of the latter category but, at the same time, silver stands here as an exception in that I not only do not recommend the application of this process to the noble metals but also that I expressly exclude from all the appended claims all noble metals. It will, therefore, be understood, that I do not contemplate the use of the process of this invention on any noble metal except silver or on any metal with any acid which readily or continuously attacks that metal. As those skilled in the art well know, the alkali metals are readily corroded by water alone and, much more readily by all acid solutions; and iron, aluminum and zinc are readily and continuously corroded by hydrochloric, sulphuric, nitric and hydrofluoric acids, but not by acetic, formic and phosphoric acids. It is also well known that chromium, lead, nickel, cobalt, antimony, tin, cadmium, and molybdenum are quite resistant to corrosion by hydrochloric, sulphuric, nitric and hydrofluoric acids and are even more resistant to corrosion by acetic, formic and phosphoric acids. It is also well known that copper is quite resistant to corrosion by hydrochloric, hydrofluoric, acetic, formic and phosphoric acids, but is readily corroded by sulphuric and nitric acids.

It is also well known that metals which are readily corroded by certain acids are quite resistant to those acids when alloyed with other metals. For example, iron, which is readily attacked by sulphuric acid, becomes very resistant to corrosion by that acid when alloyed with nickel and chromium to form stainless steel; also copper, which is readily corroded by sulphuric acid, becomes quite resistant to corrosion when alloyed with nickel to constitute Monel metal.

Accordingly, the expression "normally very resistant to corrosion," as used in this specification and particularly in some of the appended claims, is intended to exclude from the scope of the claims in which it appears all metals and alloys which, when treated with a particular acid, are readily and continuously corrodable by that acid; and to include within the scope of the claims in which the aforesaid expression appears those metals and alloys which, when treated with a particular acid, are not readily corrodable. As a specific illustration, this expression excludes from the claims in which it appears iron when treated with any of the above-mentioned inorganic acids; but includes iron when treated with any of the foregoing organic acids. It will therefore be understood that I do not contemplate the use of the process of this invention on (1) alkali metals and similar metals and alloys; (2) and all of the noble metals except silver; and (3) iron, steel, aluminum and zinc which exhibit no substantion resistance to corrosive attack when used with solutions of hydrochloric, sulfuric, nitric and hydrofluoric acid. These metals and alloys of (1) and (2) are expressly entirely excluded while the metals of (3) are expressly excluded when used with the specified mineral acids, from the appended claims by the expression "corrosion resistant."

As indicated above, however, the present method may be successfully applied to metal compounds to convert them into other compounds which may be desired as end products or as a means for accomplishing an easy and economical separation of various metal values, as will subsequently be described in more detail.

The acid selected for use in the process should be one which will produce the desired salt of the metal employed. For instance, where nickel sulphate is desired as a reaction product, sulphuric acid should be used and no hydrochloric acid or other acid, which could interfere with the desired reaction, should be present in the reaction mixture. Similarly, if nickel chloride is desired, hydrochloric acid should be the only effective acid present in the reaction mixture. A mixture of nickel salts such as sulphate or chloride may be produced in the same operation and simultaneously, in accordance with this invention, where a mixture of acids is present in the reaction mixture during the corrosion phase of the process. Where a metal sulphide rather than a metal salt (in the sense that the term "salt" has been used above and in the appended claims) is to be produced, as in the case of treatment of the copper-mercury amalgams, the acid used may be any one or more of those disclosed above, the initial concentration of the acid being the important consideration in such case, assuming other factors such as temperature and pressure to be constant.

As applied to a physical mixture of nickel and copper or to Monel metal on a commercial scale, my process is suitably carried out in a lead-lined receptacle and the metal in comminuted forms such as turnings, clippings, stampings, wire, screen, etc., is introduced into a solution of water and sulphuric acid contained in the vessel. A large proportion of metal surface for reaction is thereby provided and the corroding action of the solution approaches the theoretical maximum effectiveness. The acid which I have employed with consistent success is concentrated commercial sulphuric acid 1.83 specific gravity and I have incorporated it in the proportion of 45% by weight of such acid to water, the proportion of the metal or alloy by weight to the acid and water solution being approximately 20% to 50%.

The reaction vessel is equipped with steam coil heating means and the reaction mixture, comprising the acidic solution and the comminuted metal, is maintained at approximately the boiling point temperature of the solution, this temperature varying somewhat as the amount of nickel salt dissolved therein varies as the corrosion reaction progresses.

I have found that a very rapid rate of corrosion is realized by adding to the water, at the beginning of the operation, two-thirds of the 45% proportion by weight of concentrated sulphuric acid, or 30% by weight of such acid to water, and by adding the additional 15% by weight to the boiling solution when the proportion of sulphuric acid therein has been reduced to approximately 15%, which addition will bring the proportion of acid to the solution to its original proportion of 30% by weight, it being noted further that additional water will be added to the solution to maintain the volume of the latter substantially constant despite the loss by evaporation due to boiling. Because of the fact that the 30% by weight of sulphuric acid is incorporated in a solution which is maintained at boiling point, there will be no danger that the acid will produce more nickel sulphate by its reaction on the nickel of the alloy than can be held in solution while the latter is hot.

During the boiling operation, the reaction mixture is kept saturated with sulphur dioxide, or a suitable solution of the same, by causing the gas or solution to be introduced in such manner as to distribute it as widely and as intimately as possible in contact with the metal or alloy. Owing to the fact that the sulphur dioxide cannot remain long in the boiling reaction mixture into which it is introduced, its reaction upon the copper of the metal mixture or alloy must be practically instantaneous, and therefor its supply to the bath must be ample and constantly maintained; in fact, it will be difficult to supply more sulphur dioxide than adequate to form copper sulphide with the copper constituent of the nickel-copper mixture or alloy.

Although my process will proceed without air being present in or in contact with the reaction mixture, I have found it advisable to supply air to the said mixture in a controlled amount, at a controlled velocity, and in a manner which will enable the air to be distributed as intimately as possible through the mixture for intimate contact with the metal or alloy.

The air employed in this manner functions, I believe to keep the surfaces of the alloy particles swept substantially clean of accumulations of reaction products, particularly the solid phase products, and assists in agitating the reaction mixture to maintain a substantially uniform acid concentration throughout said mixture. Also, I believe that the oxygen in the air augments that derived by analysis of the sulphur dioxide in the reaction mixture and reacts with nickel of the metal mixture or alloy forming nickel oxide as an intermediate product, which is almost immediately converted to nickel sulphate upon hydrolysis and reaction with the sulphuric acid in the solution. Care, however, should be exercised in the use of air in the reaction mixture in this manner because it is possible to oxidize copper sulphide to copper sulphate and as soon as copper sulphate appears in any detectable amount in the reaction mixture, the corrosion reactions materially abate or cease, apparently because of catalytic poisoning, the mixture of metals or the Monel metal presumably exerting a catalytic effect on the analysis of the sulphur dioxide in the acidic reaction solution. The rate at which air is delivered into and through the reaction mixture consequently should be controlled to avoid the formation of copper sulphate in this manner. Different equipment will require different air-flow conditions, and temperature will also have an effect upon fixing maximum air tolerance. Therefore, routine experiments should be carried out to determine suitable

or optimum conditions before new equipment or new reaction mixtures are put into full scale commercial use. In the event that copper sulphate is formed, the air supply should be temporarily shut off and the reaction mixture stagnated until the copper sulphate deteriorates to the sulphide. Alternatively, the mixture may be gassed thoroughly with hydrogen sulphide to effect conversion of the copper sulphate to copper sulphide, whereupon the metal or alloy corrosion reactions may again proceed and air may be introduced into the mixture in a limited quantity.

The foregoing treatment should be continued until the sulphuric acid in the reaction mixture shall have been exhausted or substantially exhausted, the time required for such treatment having been found by me to approximate sixteen hours in the better commercial practice of this invention. When the sulphuric acid in the mixture shall have been so exhausted, the supply of sulphur dioxide and air should be turned off and the mixture be allowed to continue to boil to expel any sulphur dioxide that may remain therein. The mixture is then filtered and the precipitate of copper sulphide is washed thoroughly and set aside for the preparation therefrom of metallic copper or desirable copper chemicals. The filtrate (mainly nickel sulphate), which is slightly acidic, can be treated with hydrogen sulphide to precipitate therefrom any copper that may be therein as copper sulphate, or it can be passed over nickel turnings, thereby to cement out the copper. The filtrate will be thus purified of any "tramp" copper, i. e. copper values picked up as an impurity from equipment during handling.

The filtrate, which consists essentially of nickel sulphate, may, if desirable, be subjected to any of the well known treatments whereby it will be converted into other nickel salts; or metallic nickel may be recovered therefrom by any of the well known processes.

By the use of sulphur dioxide in the above-described process, I am enabled to sulphide the copper constituents of the nickel-copper mixtures or alloys and thereby make the production of copper sulphide, and the recovery of copper or the production of other copper compounds therefrom, a commercially profitable proposition while at the same time accomplishing the recovery of nickel sulphate from said mixtures or alloys.

The variations in proportions of the acid and water solution to metal or alloy as given hereinbefore are based upon the assumption that the metal or alloy is placed within a receptacle in a divided or discrete condition. However, if the metal or alloy is in the form of large masses, such as bars and plates, obviously the proportion of the acid and water solution to metal or alloy should be correspondingly increased; and where the process is carried on in a reaction tower wherein the acid and water solution flows over the metal or alloy, a still greater proportion of acid and water solution to metal or alloy should be employed and in such application of my process I would preferably employ a constant 30% by weight to water solution of acid.

I am aware that a number of processes have been evolved for the recovery of nickel from nickel-copper alloy waste or scrap but, so far I am advised, none of these processes has gone into extensive commercial use, principally because of their prohibitive cost. By the process set forth herein, both nickel and copper and or their salts can be separated from nickel-copper alloys and at a cost which renders the process capable of commercial adoption.

I have also found that my process, as set forth at length hereinbefore, can be advantageously employed for the production of nickel sulphate from metallic nickel and will greatly reduce the time which has been requisite heretofore for the corrosion of the nickel and the production therefrom of nickel sulphate.

In carrying out this process separately on cobalt or

brass rather than nickel or Monel metal, I have successfully followed the procedure outlined above, using cobalt or brass turnings and employing a sulphuric acid solution to make up the reaction mixture with the turnings, the concentration of the acid amounting to about 45% by weight as before. The proportion of cobalt or brass to the acid and water solution amounted to about 40% by weight at the beginning of the reaction. Sulphur dioxide gas was introduced into the lower portion of the reaction vessel well beneath the surface of the mixture at the same time that steam was introduced into the steam coils of the lead-lined vessel. The corrosion reactions began immediately thereafter and increased in rate up to the time that the boiling point temperature of the resulting mixture was reached. As before, no attempt was made to maintain super-atmospheric pressure on the reaction mixture. Rather the reaction vessel was left open and the fumes evolved from the mixture were vented through a stack open to the atmosphere. Air was introduced into the reaction mixture under controlled circumstances, as described above, beginning at approximately the same time that the sulphur dioxide flow was started and continuing throughout the reaction period.

When the concentration of the sulphuric acid in the reaction mixture diminished to about 30% by weight of the acid to the cobalt sulphate or the zinc sulphate solution, an additional 15% by weight of the concentrated acid of 1.83 specific gravity was added. No further additions of acid were made and the heating and gassing of the reaction mixture was continued until the cobalt or brass and acid therein were virtually exhausted. A total of 16 hours was required to carry the corrosion reactions to completion whereupon residual sulphur dioxide of the mixture, after the supply of gas to the mixture has been cut off, was boiled out and the elemental sulphur was separated from the mixture consisting primarily of cobalt sulphate and water in any suitable manner. Where brass instead of cobalt was used the mixture was filtered, following boiling to expel residual sulphur dioxide, and the copper sulphide was thoroughly washed, while the filtrate consisting primarily of zinc sulphate and water is collected for further treatment.

I have also successfully treated finely-divided chromium in the manner described above, a phosphoric acid solution being employed with the object of producing a chromium phosphate solution. The starting solution was prepared by adding 125 cc. of 85% orthophosphoric acid to 250 cc. of water. The chromium particles were introduced into the solution and the sulphur dioxide gas and air were delivered in equal volumes into the mixture as described above. A few moments later, heat was applied to the mixture by means of steam coils and the heating was continued until the temperature of the mixture had reached 90° C., and flow of air and sulphur dioxide was continued until the chromium was virtually exhausted at the end of about 7 hours. The reaction mixture was subjected to atmospheric pressure throughout the reaction period. The elemental sulphur in the solution was separated and removed from the liquid phase of the mixture which contained substantial quantities of chromium phosphate.

I have also successfully treated Chromel wire in the manner generally described above, a 25% sulphuric acid solution being used as the starting solution. A total of only 2 hours was required for complete conversion of metal values in one of these Chromel treatments where only 82.5 grams of fine standard Chromel wire was used. The temperature of the reaction mixture at the beginning of the process, when the sulphur dioxide and air was introduced into the mixture, was approximately 95° C. and the pressure of the mixture was approximately atmospheric.

In some small scale operations I have determined the suitability of still other metals, alloys and acids. In one particular trial, I prepared a mixture consisting of 400 grams of Monel turnings, 150 cc. of commercial acetic acid (glacial of about 90% strength) and 250 cc. of water. With the mixture under atmospheric pressure and at about 85° C., I introduced sulphur dixoide thereinto at the rate of about one bubble per second, and introduced air thereinto at about one-half that rate. The corrosion and conversion of the Monel metal was complete at the end of 2½ hours. Nickel acetate and copper sulphide were the reaction products, all the nickel acetate being dissolved in the reaction mixture and all the copper sulphide being in the solid phase as a sludge-like mass on the bottom of the reaction vessel.

Using a commercial hydrochloric acid of about 28% strength, I have successfully practiced the process of this invention by making a reaction mixture of this acid and about four times its volume of pure water, and adding thereto Monel metal turnings. The volume of the reaction mixture and the amount of Monel metal approximated that stated in the above acetic acid example. With the reaction mixture at approximately 95° C., sulphur dioxide was introduced into the mixture and within about 2½ hours corrosion of the Monel metal was complete and the entire nickel value thereof was contained in the liquid phase of the reaction mixture as nickel chloride, while substantially all the copper thereof existed as copper sulphide sludge.

In another relatively small scale operation, I successfully tested the suitability of nitric acid in this process, cadmium metal being used in one test and Monel metal being used in another test. In each case approximately 400 grams of metal were used and the nitric acid was diluted to about 25% strength to make up the reaction mixture. Sulphur dioxide and air were again delivered into the mixture continuously, resulting in the formation of cadmium nitrate and elemental sulphur in one instance and copper sulphide and nickel nitrate in the other, the said nitrates being dissolved in the liquid phase of the reaction mixture, thus enabling easy and sharp separation of the metal values. Unlike the previous examples in this case, the reaction mixture was maintained at about room temperature, i. e. about 20° C. to about 30° C. throughout the reaction period.

To determine further the effectiveness of phosphoric acid in the process of this invention, I added 125 cc. of 85% orthophosphoric acid to 250 cc. of water, introduced into the resulting solution 400 grams Monel metal turnings, and then promptly turned sulphur dioxide gas and air in equal volumes into the mixture. Seven minutes later, heat was applied to the mixture by means of steam coils in the reaction vessel and the liquid phase of the mixture by this time has turned milky. When the solution temperature reached 42° C. it took on a greenish color. The heating was continued until the temperature of the mixture reached 98° C. After one hour, during which the temperature was maintained substantially constant at 98° C. and gassing with sulphur dioxide and air was continued, the supply of sulphur dioxide and air to the mixture was cut off and I determined that 40% of the original acid content of the mixture was exhausted. I then filtered the solution, boiled the filtrate to expel the sulphur dioxide, and tested the filtrate for copper, finding that it contained none. A test of the filtrate for sulphate formation also proved negative. The nickel phosphate product, being soluble in aqueous acids, was contained in substantial quantity in solution in the filtrate because of the presence of free phosphoric acid therein.

In another set of experimental operations, I mixed in two batches 120 cc. of 50% hydrofluoric acid with 280 cc. of water and to one batch I added 400 grams of cobalt scrap and to the other batch I added 400 grams of Monel metal turnings. Sulphur dioxide gas and air were turned into the resulting mixture promptly thereafter and heat was applied thereto, as described above, beginning five minutes after the gassing was started. The solution in contact with the cobalt scrap was milky

throughout substantially the entire reaction period of one hour and the temperature thereof was maintained between 75° and 90° C. during this time. The temperature of the cobalt reaction medium was maintained between about 40° C. and about 60° C. throughout the reaction period. When the gassing of the Monel metal mixture was discontinued at the end of the hour, I determined that two-thirds of the hydrofluoric acid had been consumed and on testing the liquid phase of the reaction mixture for copper, I found none. A test for sulphate formation on the liquid phase of this Monel metal reaction mixture also proved negative. A similar test for sulphates on the cobalt scrap mixture proved negative and it was found that the cobalt fluoride in solution was stoichiometrically equivalent to the cobalt scrap consumed in the process.

Formic acid was tested in the same general manner, 150 cc. of 90% formic acid being added to and mixed with 250 cc. of water, and 400 grams of Monel turnings being introduced into the solution, gassing of the resulting mixture with sulphur dioxide and air in equal volumes being begun immediately thereafter. The temperature of the mixture during the reaction period of about one hour was maintained about 85° C., during which time approximately one-half of the original acid content of the mixture was consumed. A test of the liquid phase of the final mixture for copper and another test thereof for sulphate formation proved negative. The nickel formate product was contained in solution in liquid phase of the mixture.

In a parallel experiment wherein the same reagents and conditions were employed, except that nickel was used instead of Monel metal, similar results were obtained. The nickel formate product proved to be free from sulphate contamination and was distributed between the liquid and the solid phase due to its limited solubility.

In still another small scale operation, I prepared a mixture consisting of 400 grams of zinc turnings, 150 cc. of commercial acetic acid (glacial of about 90% strength) and 200 cc. of water. With the reaction mixture under atmospheric pressure and at about 85° C., I introduced sulphur dioxide thereinto at the rate of about one bubble per second and I introduced air thereinto at about one-half that rate. The corrosion and conversion of the zinc was visibly rapid and was virtually complete within about two and one-half hours. The zinc acetate in solution in the reaction mixture was the primary reaction product although a certain amount of finely-divided sulphur in sludge-like form collected on the bottom of the reaction vessel when the mixture was permitted to stand.

I similarly tested the conversion of iron to produce iron acetate in accordance with this invention process, using 400 grams of iron turnings, 150 cc. of commercial acetic acid and 250 cc. of water, as stated in the foregoing example. The introduction of sulphur dioxide and air in the reaction mixture was carried out as specified immediately above and the results were virtually the same in that reaction was complete at the end of about four and one-half hours. The iron acetate product was contained in the reaction solution while a semi-colloidal sulphur sludge was accumulated on the bottom of the vessel.

In still another experimental run, I introduced finely-divided nickel into a solution of hydrochloric acid of about 28% strength, diluted to about four times its volume with pure water. Sulphur dioxide gas and air were turned into the mixture and heat was applied to it as described above, beginning about five minutes after the gassing was started. The temperature of the solution was maintained between about 75° C. and 90° C. throughout the reaction period. The gassing of the mixture was discontinued on substantial exhausion of the metallic nickel. The amount of nickel chloride contained in solution in the reaction mixture proved to be stoichiometrically equivalent to the amount of nickel charged to the vessel and reacted therein. The solid phase of the reaction mixture consisted essentially of semi-colloidal sulphur which collected on the bottom of the reaction vessel and was readily separated from the liquid portion of the said mixture.

To study the effects of pressure of the present process, I prepared a reaction mixture of about 250 grams of Monel metal, 40 cc. sulphuric acid (commercial 1.83 specific gravity) and 210 cc. of pure water. With a pressure of 30 pounds per square inch gauge, on the reaction mixture and the temperature of the mixture at 85° C., I introduced air and sulphur dioxide gas into the mixture at the same rates and in equal volumes for a period of three hours. At the end of this time, corrosion of the Monel metal was essentially complete and the metal values thereof existed as nickel sulphate in solution and copper sulphide in sludge form.

In an experiment carried out upon a complex alloy, the objects and advantages of this invention as set forth above were fully realized. The alloy employed contained in substantial amounts, copper, lead, tin, zinc, silver, and iron and was one which hitherto has resisted all efforts to obtain rapid corrosion and subsequent easy and sharp separation of its metal values. The reaction mixture employed consisted essentially of 400 grams of this alloy dispersed in a solution of 60 cc. of sulphuric acid (commercial 1.83 specific gravity) in 315 cc. of water. With the temperature of the reaction mixture at about 95° C. and the mixture under substantially atmospheric pressure, sulphur dioxide and air were introduced continuously thereinto for a period of approximately three hours. At the end of this period, the corrosion of the alloy was essentially complete and the lead, iron, zinc and tin compounds of the alloy existed as sulphates; and the copper and silver compounds existed as sulphides, the iron, zinc and tin compounds being dissolved in the reaction mixture solution and the other derivatives being in the solid phase.

The degree of subdivision of the metal to be corroded and converted has a considerable bearing upon the rate of the corrosion reactions, consequently, the times set forth above may be much longer or shorter than those which may be obained tusing, as starting materials, metals or alloys of somewhat different piece size. For instance, instead of 24 hours being required for complete corrosion of Monal metal, a total of 5½ or 10 hours may be sufficient if the material is reduced to an extremely fine subdivision condition.

This matter of the condition of the starting material carries over with other facts described above such as acid concentration, temperature and pressure to the practice of the invention as applied to metal compounds such as nickel sulphide-tungsten sulphide.

In an experiment carried out on a laboratory scale, I treated 100 grams of this mixed sulphide material in somewhat comminuted form with aqueous sulphuric acid, bubbling sulphur dioxide gas into the acid solution while the temperature of the solution was maintained at approximately 90° C. The sulphuric acid solution was prepared by mixing 49.5 grams of 66° Bé. acid with 100 cc. of water. Air was also bubbled into the solution as described above at about the same rate and in about the same amount as the sulphur dioxide. Within about six hours, the conversion of the nickel sulphide to nickel sulphate was virtually complete and a good separation of tungsten sulphide as a sludge was obtained by decanting off the liquor and filtering and washing the residue of the reaction mixture.

In a similar experiment on this mixed sulphide material I introduced an acid solution into a reaction vessel of the type described above and containing 100 grams of nickel sulphide-tungsten sulphide, this solution containing 75 cc. of hydrochloric acid of 28% strength by weight and 77 cc. of water. While maintaining the mixture un-

der substantially atmospheric pressure and maintaining the temperature of the mixture at approximately 90° C., I continuously bubbled air and sulphur dioxide gas into the solution in about equal volumes for a period of three hours. At the end of this time, the reaction ceased due to exhaustion of the acid, and I filtered the liquor from the residue, determining that the liquid phase contained in solution the nickel chloride product, while the tungsten sulphide product existed in the form of a sludge and constituted part of the residue. The separation of the nickel and tungsten values was substantially as sharp as, and yields of reaction of products were substantially as great as those stated in the foregoing example.

I have furthermore carried out this invention on various metals, metal alloys, and materials containing metals in the form of compounds, with acids of initially comparatively very low strength. It will be understood, however, that generally operations of this type will not be found very practical or commercial because of the small yields of desired products due to the rapid exhaustion of the acid available for reaction.

Nitric acid of about 0.5% strength by weight was tested as generally described above and found to operate successfully, producing detectable amounts of the desired metal compounds. In one typical experiment I used 250 cc. of an aqueous nitric acid solution of 0.5% strength, adding it to 250 grams of brass turnings contained in a typical reactor of the type described above and turning sulphur dioxide gas and air in substantially equal volumes into the mixture and gassing it for a period of 30 minutes. The experiment was carried out with the mixture under atmospheric pressure, but the temperature of the mixture was allowed to rise from its initial room temperature as exothermic heat was generated. At the end of this period the acid was substantially exhausted and the reaction virtually ceased, although some brass was left unreacted. The zinc of the portion of the brass reacted was found in solution in the form of zinc nitrate, while the copper of that portion was in the form of copper sulphide sludge.

Sulphuric acid likewise proved to be effective in this small concentration, the experiment being carried out again with 250 grams of brass and 250 cc. of 0.5% strength by weight, sulphuric acid making up the starting mixture. In this experiment, however, heat was applied to the mixture and its temperature was raised to 95° to 100° C., prior to the introduction of the sulphur dioxide gas and air thereinto. This temperature was maintained throughout the 30 minute gassing period. On analysis, the zinc portion of the brass reacted was in the form of zinc sulphate, substantially none of which was found in solution due to the exhaustion of the acid; and the copper was in the form of copper sulphide sludge.

A solution of 0.5% strength by weight of formic acid was used in this same way, being applied, however, to Monel metal turnings rather than brass, and it was found that the results obtained corresponded to those described in the above examples. Nickel formate was formed in relatively small amount, but in proportion to the quantity of acid used, during the 30 minute reaction period; and the copper was converted to sulphide and collected as a sludge. The temperature and pressure conditions were substantially as defined above in connection with the discussion of the experiment on the 0.5% sulphuric acid solution.

Acetic acid likewise proved to be effective in this very small initial concentration as determined in an experiment carried out as described above with reference to this 0.5% sulphuric acid solution. Monel metal was used in this operation and nickel acetate and copper sulphide were the reaction products. The temperature and pressure conditions were the same as those in the said sulphuric acid test.

In still another experiment, hydrofluoric acid was found to be effective in this very low initial concentration and zinc fluoride and copper sulphide were formed, brass being used instead of Monel metal. Again, the temperature and pressure circumstances were those described in the said sulphuric acid experiment.

A solution (250 cc.) of 0.5% strength by weight of hydrochloric acid was gassed with sulphur dioxide for 30 minutes, the solution temperature being maintained between about 80° C. and about 100° C. Monel metal turnings (250 grams) mixed in the solution prior to the gassing were corroded appreciably and nickel chloride and copper sulphide were formed in appreciable amounts, the nickel salt being dissolved in the liquid phase of the reaction mixture and the copper sulphide existing as a slude-like accumulation on the bottom of the reactor. The acid was essentially exhausted at the end of the gassing period and the metal corrosion reactions had apparently ceased by that time.

Phosphoric acid was used in this same manner and found to be effective in low concentration. A solution (250 cc.) of phosphoric acid of 0.5% strength by weight was poured into a reactor of the type described above, containing 250 grams of brass turnings and the resulting mixture was heated to about 95° C. Sulphur dioxide gas was then bubbled into the solution continuously for a period of about 30 minutes, at the end of which time the reactions appeared to have ceased and the acid content of the mitxure was substantially exhausted. Zinc phosphate and copper sulphide produced in the reaction mixture through the metal corrosion reactions going on during the gassing period were separated together as a sludge from the liquid phase of the said reaction mixture.

In order to determine the applicability of this process of my invention to metals standing below hydrogen in this series, I carried out several experiments described below using various of the acids set forth above and employing sulphur dioxide in all instances and air in certain cases and imposing pressure on the reaction mixture during the reaction period in one instance.

Using finely-divided antimony metal and a 25% sulphuric acid solution, I contacted sulphur dioxide with the metal in the acid solution in the manner described above, continuously running the sulphur dioxide gas into the bottom of the vessel, while maintaining the temperature of the gas mixture throughout substantially the entire reaction period at approximately 90° C. and maintaining the pressure at approximately atmospheric. The reaction appeared to go to completion and exhaustion of the available antimony metal in a matter of about four and one-half hours, approximately 80 grams of metal having been charged initially. The antimony was converted in this reaction to the sulphide which collected on the bottom of the reaction vessel as a sludge-like mass which was easily separated from the mixture by filtration.

In a similar test I used copper in finely-divided form, introducing it into a solution of hydrochloric acid of about 28% strength and diluted to about four times its volume with pure water. The available copper charged to the mixture this way was substantially completely converted to copper sulphide in about six and one-half hours, during which time sulphur dioxide was continuously introduced into the mixture and the temperature of the mixture was maintained at approximately 95° C. The copper sulphide was collected as a sludge which settled from the liquid phase of the mixture and was readily separated therefrom.

In a similar test using tungsten in finely-divided form and phosphoric acid, I produced tungsten sulphide as a sludge-like product which collected on the bottom of the vessel. Substantially complete exhaustion of the mixture of available tungsten metal in about five and one-half hours, during which time sulphur dioxide and air in equal volumes were bubbled into the bottom of the reaction vessel. The phosphoric acid solution was prepared as

described above, 125 cc. of 85% orthophosphoric acid being diluted with 250 cc. of water and 400 grams of tungsten was charged into the resulting solution to make the starting mixture.

Molybdenum sulphide was produced in a similar experiment, the corrosion reaction proceeding rapidly in an acetic acid solution prepared by diluting 200 cc. of commercial glacial acid with 200 cc. of water. Into the resulting acid solution 400 grams of molybdenum metal in finely-divided form was charged. The reaction period was five and one-half hours, during which time sulphur dioxide and air were introduced continuously at the rate of one bubble per second in each instance. However, throughout this reaction period, a pressure of 30 lbs. per square inch gauge was maintained on the reaction mixture. Close observation of the reaction, however, indicated that the reaction did not proceed any more rapidly in this case than in any of the foregoing where atmospheric pressure was applied throughout the period to the reaction mixture.

In still another test, I have successfully used nitric acid to effect the corrosion of antimony metal to produce the result and advantages of this invention stated above. In this test, approximately 400 grams of antimony was charged into nitric acid diluted to about 25% strength and sulphur dioxide and air were bubbled continuously into the resulting reaction mixture at a rate of about one bubble per second. The corrosion of the antimony and the production of antimony sulphide proceeded at a relatively rapid rate until substantially all the available antimony metal was converted in a matter of about four and one-half hours. The antimony sulphide accumulated on the bottom of the vessel as a sludge-like mass and was easily separated from the reaction mixture.

To test the effectiveness of the method of this invention as applied to a physical mixture consisting of metals below hydrogen in the series, I employed finely-divided copper metal and antimony metal, introducing these metals into a solution of hydrochloric acid of about 28% strength diluted to about four times its volume with pure water. The available copper and antimony charged to the mixture were substantially completely converted to the respective sulphides in about six and one-half hours, during which time sulphur dioxide was continuously bubbled into the mixture and the temperature of the mixture was maintained at approximately 90° C. The copper sulphide and antimony sulphide were collected as a sludge which settled from the liquid phase of the mixture and was easily separated therefrom.

Nitric acid of about 5.0% strength by weight was tested as generally described above and found to operate successfully producing detectable amounts of the desired metal compounds. In one typical experiment, I used 250 cc. of an aqueous nitric acid solution of 5.0% strength, adding it to 250 grams of a physical mixture of zinc and copper contained in a typical reactor of the type described above and turning sulphur dioxide gas and air in substantially equal volumes into the mixture and gassing it for a period of thirty minutes. The experiment was carried out with the mixture under atmospheric pressure, but the temperature of the mixture was allowed to rise from its initial room temperature as exothermic heat was generated. At the end of this period, the acid was substantially exhausted and the reaction virtually ceased, although some of the metal mixture was left unreacted. The zinc of the portion of the metal mixture reacted was found in solution in the form of zinc nitrate, while the copper of that portion was in the form of copper sulphide sludge.

Sulphuric acid likewise proved to be effective in this small concentration, the experiment being carried out again with 250 grams of a physical mixture of copper and zinc and 250 cc. of 5.0% strength by weight, sulphuric acid making up the starting mixture. In this experiment, however, heat was applied to the mixture and its temperature was raised to 95° to 100° C., prior to the introduction of the sulphur dioxide gas and air thereinto. This temperature was maintained throughout the thirty minutes gassing period. On analysis, the zinc portion of the metal mixture reacted was in the form of zinc sulphate in solution; and the copper was in the form of copper sulphide sludge.

A solution of 5.0% strength by weight of formic acid was used in this same way, being applied, however, to a nickel-copper mixture rather than to a physical mixture of copper and zinc, and it was found that the results obtained corresponded to those described in the above examples. Nickel formate was formed in relatively small amount, but in proportion to the quantity of acid used, during the thirty minute reaction period; and the copper was converted to sulphide and collected as a sludge. The temperature and pressure conditions were substantially as defined above in connection with the discussion of the experiment on the 5.0% sulphuric acid solution.

Acetic acid likewise proved to be effected in this very small initial concentration as determined in an experiment carried out as described above with reference to this 5.0% sulphuric acid solution. A nickel-copper mixture was used in this operation and nickel acetate and copper sulphide were the reaction products. The temperature and pressure conditions were the same as those in the said sulphuric acid test.

In still another experiment, hydrofluoric acid was found to be effective in this very low initial concentration and zinc fluoride and copper sulphide were formed, a physical mixture of zinc and copper being used instead. Again, the temperature and pressure circumstances were those described in the said sulphuric acid experiment.

A solution (250 cc.) of 5.0% strength by weight of hydrochloric acid was gassed with sulphur dioxide for thirty minutes, the solution temperature being maintained between about 80° C. and about 100° C. A physical mixtures of nickel and copper (250 grams) added to the solution prior to the gassing were corroded substantially and nickel chloride and copper sulphide were formed in appreciable amounts, the nickel salt being dissolved in the liquid phase of the reaction mixture and the copper sulphide existing as a sludge-like accumulation on the bottom of the reactor. The acid was essentially exhausted at the end of the gassing period and the metal corrosion reactions had apparently ceased by that time.

Phosphoric acid was used in this same manner and found to be effective in low concentration. A solution (250 cc.) of phosphoric acid of 5.0% strength by weight was poured into a reactor of the type described above, containing 250 grams of a physical mixture of copper and zinc and the resulting mixture was heated to about 95° C. Sulphur dioxide gas was then bubbled into the solution continuously for a period of about thirty minutes, at the end of which time the reactions appeared to have ceased and the acid content of the mixture was substantially exhausted. Zinc phosphate and copper sulphide produced in the reaction mixture through the metal corrosion reactions going on during the gassing period were separated together as a sludge from the liquid phase of the said reaction mixture.

In each of the foregoing examples where the initial acid concentration of the reaction mixture amounted to approximately 5%, a test performed at the end of the reaction period showed in every instance that the acid concentration at the time that the reactions of this invention apparently ceased was approximately 0.5%, indicating the criticality of this minimum acid value in reaction mixtures of this invention, as set out above.

Since, as stated above, this invention is based upon my discovery that certain desirable reactions take place

and certain valuable products are obtained when various particular materials are brought together under favorable circumstances, the important thing is to have the said materials together for as long as necessary to permit the said reactions to go forward. The manner of bringing the materials together or the order of their addition to a reaction vessel or a reaction medium thus will be generally of incidental importance.

This is a continuation-in-part of my copending application, Serial No. 332,553, filed January 21, 1953.

Having thus described the present invention so that others skilled in the art may understand the same, I state that what I desire to obtain by Letters Patent is set out in what is claimed.

What is claimed is:

1. The method of rapidly and economically converting a corrosion resistant alloy of at least one metal above and at least one metal below hydrogen in the electromotive force series into metal compounds which comprises the steps of introducing a corrosion resistant alloy containing said metals into an aqueous solution containing in excess of about 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid, phosphoric acid, and passing sulphur dioxide into the solution, whereby the insoluble sulphides are precipitated and the soluble salts of the acid selected are retained in the solution.

2. The method of economically converting a corrosion resistant alloy of at least one metal above and at least one metal below hydrogen in the electromotive force series into metal compounds which comprises the steps of introducing said alloy into a solution containing in excess of about 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid and phosphoric acid, at a temperature between about 80° C. and 100° C. and passing sulphur dioxide into the solution, whereby the insoluble sulphides are precipitated and the soluble salts of the acid selected are retained in the solution.

3. The method of rapidly and economically converting a corrosion resistant alloy of at least one metal above and at least one metal below hydrogen in the electromotive force series into metal compounds which comprises the steps of introducing said alloy into an aqueous solution containing in excess of about 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid, and phosphoric acid, passing sulphur dioxide into the solution and simultaneously bubbling air into said solution whereby the insoluble sulphides are precipitated and the soluble salts of the acid selected are retained in the solution.

4. The method of rapidly and economically converting a corrosion resistant alloy of at least one metal above and at least one metal below hydrogen in the electromotive force series into metal compounds which comprises the steps of introducing said alloy into an aqueous solution containing in excess of about 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid and phosphoric acid, at a temperature between about 80° and 100° C. passing sulphur dioxide into the solution and simultaneously bubbling air into said solution, whereby the insoluble sulphides are precipitated and the soluble salts of the acid selected are retained in the solution.

5. The method of preparing metal compounds from a corrosion resistant alloy of a metal above and a metal below hydrogen in the electromotive force series which comprises introducing the alloy into a solution of at least 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid, and introducing sulphur dioxide into the solution.

6. The method of rapidly, economically and sharply separating values of metal above hydrogen in the electromotive force series from values of another metal below hydrogen in said series which comprises the steps of introducing a corrosion resistant alloy containing said metals into an aqueous solution containing in excess of about 0.5% by weight of an acid, selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, hydrochloric acid, nitric acid and phosphoric acid, and passing sulphur dioxide into the solution thereby forming a soluble salt of the selected acid of a metal above hydrogen and an insoluble sulphide of a metal below hydrogen and separating and removing the sulphide as a solid from the liquid phase of the reaction mixture containing said soluble salt.

7. The method of preparing metal compounds from an alloy which consists in introducing into a solution of at least 0.5% by weight of sulphuric acid an alloy which is normally very resistant to corrosion by said solution, passing sulphur dioxide into the solution and reducing said sulphur dioxide until a major part of the alloy has been converted into metal compounds, and recovering the resulting compounds from the reaction mixture.

8. A method of preparing metal compounds from corrosion resistant alloys of at least one metal above and at least one metal below hydrogen in the electromotive force series which consists in introducing the alloy into a solution at a temperature between about 80° C. and 100° C. containing at least 0.5% by weight of hydrochloric acid and passing sulphur dioxide into the solution thereby giving a solution of a soluble chloride and a precipitate of the insoluble sulphide.

9. The method of preparing metal compounds from corrosion resistant alloy of at least one metal above and at least one metal below hydrogen in the electromotive force series which consists in introducing the alloy into a solution at substantially room temperature and containing at least 0.5% by weight of nitric acid, passing sulphur dioxide into the solution and simultaneously bubbling air into said solution, the sulphur dioxide and air being delivered into the solution in substantially equal volumes and at substantially the same rate, thereby giving a solution of a soluble nitrate and a precipitate of the insoluble sulphide.

10. A process for the manufacture of nickel sulphate and copper sulphide from a nickel copper alloy which comprises introducing said alloy into a continuously bubbling aqueous sulphuric acid bath containing at least 0.5% by weight of sulphuric acid, and passing sulphur dioxide into said bath and into contact with said alloy, whereby copper sulphide is precipitated and nickel sulphate obtained in the solution.

11. In the process set forth in claim 10, delivering air continuously into the said bath simultaneously with the sulphur dioxide.

12. The method of rapidly, economically and sharply separating the copper values from the nickel values of Monel metal which comprises the steps of heating an aqueous sulphuric acid solution containing at least 0.5% sulphuric acid in contact with said Monel metal, bringing sulphur dioxide into said solution and forming copper sulphide and nickel sulphate, and separating and removing said copper sulphide as a solid from the reaction mixture.

13. The process for the manufacture of nickel sulphate and copper sulphide from a nickel copper alloy which comprises subjecting the said alloy, in a discrete condition, to a continuously boiling bath of a sulphuric acid dissolved in water, in the approximate proportion of 30% of acid by volume to water, delivering sulphur dioxide continuously into said bath and into contact with the said alloy therein, maintaining substantially constant the volume of the bath by addition thereto of water to compensate for the loss of water due to the boiling of the

bath, continuing the boiling of the bath until the sulphuric acid therein is substantially exhausted, and separately recovering the resulting nickel sulphate solution and the insoluble copper sulphide.

14. The process for the manufacture of nickel sulphate and copper sulphide from a nickel-copper alloy comprises subjecting the said alloy, in a discrete condition, to a continuously boiling bath of sulphuric acid dissolved in water, the approximate proportion of acid to water being 30% by volume, a portion of the acid being incorporated in the bath at the beginning of the operation and the remainder of the acid being added to the bath when the proportion of acid to the bath shall have fallen to a predetermined degree, delivering sulphur dioxide continuously into said bath and into contact with the said alloy therein, maintaining substantially constant the volume of the bath by addition thereto of water to compensate for the loss of water due to the boiling of the bath, continuing the boiling of the bath until the sulphuric acid therein is substantially exhausted, and separately recovering the resulting nickel, sulphate solution and the insoluble copper sulphide.

15. That method of forming nickel sulphate and copper sulphide from a nickel-copper alloy comprising the steps of preparing an aqueous reaction bath of concentrated sulphuric acid, associating the alloy with the bath, heating the bath to approximately its boiling temperature while the bath is retained under atmospheric pressure, maintaining the volume of the bath substantially uniform by adding water thereto at intermittent intervals, adding an additional volume of concentrated sulphuric acid to the bath after the original acid composition of the bath has been reduced by reaction of the acid, continuously passing sulphur dioxide into the bath and into contact with the alloy to sulphurize the copper and form insoluble copper sulphide therefrom, continuously passing air into the bath simultaneously with the sulphur dioxide to also contact the alloy therein, oxidizing the nickel of the alloy to form a solution of nickel sulphate therefrom, filtering the bath to obtain the copper sulphide therefrom, and thereafter recovering nickel sulphate from the filtrate.

16. A process for the manufacture of a cobalt salt and copper sulphide from a cobalt-copper alloy which comprises introducing said alloy into an aqueous solution containing an excess of about 0.5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, hydrochloric acid, nitric acid, and phosphoric acid, and passing sulphur dioxide into the solution and thereby forming a soluble cobalt salt of the selected acid and copper sulphide.

17. The method of rapidly and economically converting a metal into a compound of said metal, which comprises the steps of introducing into an aqueous solution containing in excess of about .5% by weight of a strong acid a metal which is normally very resistant to corrosion by said solution, passing therein sulphur dioxide and reducing the sulphur dioxide until the major part of the metal has been converted into a metal compound, and recovering the resulting compound from the reaction mixture.

18. A process as claimed in claim 17 wherein the aqueous solution of the acid is maintained at a temperature of about 80° C. to 100° C.

19. A process as claimed in claim 17 wherein air is simultaneously introduced into the solution with the sulphur dioxide.

20. A method of rapidly and economically converting metals standing above hydrogen in the electromotive series into a solution of said metal salts, which comprises the steps of introducing into an aqueous solution containing in excess of about .5% by weight of a strong acid metals standing above hydrogen in said series and normally very resistant to corrosion by said solution, introducing therein sulphur dioxide and reducing said sulphur dioxide in said solution until the major parts of the metals have been converted into metal salts, and recovering the resulting salts from the reaction mixture.

21. A method of rapidly and economically converting metallic cobalt into cobalt sulphate solution, which comprises the steps of introducing said cobalt into an aqueous solution containing in excess of about .5% by weight of sulphuric acid, and bubbling therein sulphur dioxide.

22. A method of preparing nickel sulphate solution from metallic nickel, which consists in introducing the nickel into a solution of at least .5% by weight of sulphuric acid, introducing sulphur dioxide into the solution, reducing the sulphur dioxide and removing the sulphur so precipitated.

23. The method of rapidly and economically converting metallic chromium into chromium salt solution which comprises the steps of introducing said chromium into an aqueous solution containing in excess of about .5% by weight of a strong acid and introducing therein sulphur dioxide, reducing the sulphur dioxide and producing elemental sulphur.

24. A method of rapidly and economically converting metallic cobalt into a solution of the salt, which comprises the steps of introducing said cobalt into an aqueous solution containing in excess of about .5% by weight of a strong acid and introducing therein sulphur dioxide, reducing the sulphur dioxide and producing elemental sulphur.

25. A method of preparing a nickel salt solution from metallic nickel, which consists in introducing said nickel into a solution of at least .5% by weight of a strong acid and introducing sulphur dioxide into the solution, reducing the sulphur dioxide and precipitating elemental sulphur.

26. The method of rapidly and economically converting metals standing below hydrogen in the electromotive series into a mixture of metal sulphides, which comprises the steps of introducing into an aqueous solution containing in excess of about .5% by weight of a strong acid metals standing below hydrogen in said series and normally very resistant to corrosion by said solution and running a stream of sulphur dioxide gas into said solution, reducing the sulphur dioxide and precipitating the insoluble sulphides.

27. The method of rapidly and economically converting a metal into a compound of said metal, which comprises the steps of introducing into an aqueous solution containing about 5% by weight of a strong acid a metal which is normally very resistant to corrosion by said solution, passing therein sulphur dioxide and reducing the sulphur dioxide until the major part of the metal has been converted to a metal compound, and recovering the resulting compound from the reaction mixture.

28. The method of rapidly and economically converting metals standing above hydrogen in the electromotive series into a solution of salts of said metals, which comprises the steps of introducing into an aqueous solution containing about 5% by weight of a strong acid metals standing above hydrogen in said series and normally very resistant to corrosion by said solution and introducing therein sulphur dioxide and reducing the sulphur dioxide until the major parts of the metals have been converted into salts of the metals, and recovering the resulting salts from the reaction mixture.

29. The method of rapidly and economically converting metals standing below hydrogen in the electromotive series into a mixture of metal sulphides, which comprises the steps of introducing into an aqueous solution containing 5% by weight of a strong acid metals standing below hydrogen in said series and normally very resistant to corrosion by said solution, running a stream of sulphur dioxide gas into said solution, reducing the sulphur dioxide and precipitating the insoluble sulphides.

30. The method of preparing metal compounds from a corrosion resistant alloy of a metal above and a metal below hydrogen in the electromotive force series which

comprises introducing the alloy into a solution of 5% by weight of an acid selected from the group consisting of formic acid, acetic acid, sulphuric acid, hydrofluoric acid, nitric acid, hydrochloric acid and phosphoric acid, and introducing sulphur dioxide into the solution.

31. A process for the manufacture of nickel sulphate and copper sulphide from a nickel copper alloy which comprises introducing said alloy into a continuously bubbling aqueous sulphuric acid bath containing 5% by weight of sulphuric acid, and passing sulphur dioxide into said bath and into contact with said alloy, whereby

copper sulphide is precipitated and nickel sulphate is obtained in the solution.

32. The method of rapidly and economically converting a nickel-chromium alloy into a solution of salts of nickel and chromium, which comprises the steps of introducing the said alloy into an aqueous solution containing about 5% by weight of a strong acid, introducing sulphur dioxide into said solution, reducing the sulphur dioxide and producing elemental sulphur.

No references cited.