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ACCELERATING ACTION OF ACIDS ON METALS

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No Drawing. Application April 27, 1953,
Serial No. 351,508

18 Claims. (Cl. 41—42)

This invention relates to dissolving metals and/or surface impurities on metals in acids. The present invention is useful in many varieties of industrial processes employing aqueous solutions of acids for treating metals. For example, in certain embodiments of the present invention, a stainless steel sheet is pickled whereby most of the scale is removed without any significant corrosion of the metal. In other embodiments of the invention, nickel plate is dissolved or stripped from a copper base by preferentially dissolving the nickel at a very rapid rate. Other applications of the present invention include the recovery of scrap-metal by dissolving components of alloys and other operations in which metals and/or surface impurities on metals are dissolved in an acid.

The present invention involves the utilization of an organic agent functioning as an activator to speed up the rate of action of the acid. The organic accelerator is slowly decomposed, but is not consumed in any kind of stoichiometric proportions and functions in the nature of a catalyst. No offensive fumes, insoluble residues, adherent films, or similar difficulties result from the use of the organic accelerators of the present invention.

The dissolving of metals in acids is one of the oldest recognized chemical reactions. During the last century, millions of man-hours have been devoted to operating industrial processes consisting essentially of dissolving metals in acids. The prior art has observed that the initial reaction rate of a metal being dissolved in acid generally has been more rapid than after the acid has acted upon the metal for a period of time. Under some conditions, the metal surface has been modified in such a way that there has been a retarding of the reaction rate of the acid on the metal. To alleviate such difficulties, prior workers have sometimes employed the combination of an acid and an oxidizing agent such as nitric acid, persulfuric acid or air for dissolving metals more rapidly. Such inorganic modifying agents have been objectionable in many instances. Heretofore, organic agents have been employed, but without great success, for modifying the reaction rate of acids as, for example, by the use of wetting agents to bring about more rapid wetting of the metal surface by the acid, by the use of viscosity modifiers, and by other methods.

According to the present invention, the reaction rate of the acid system is activated by the use of an organic material capable of functioning in a manner partaking in part of the nature of a catalyst, that is, functioning in such a way that the organic material is decomposed at a rate significantly less than if it were according to any stoichiometric chemical reaction. The present invention relates to a process of dissolving metals in an acid, to the solutions which can be utilized in the process, and to the concentrates which can be employed in preparing such solutions.

This application is a continuation-in-part of an application of Richard Springer and Walter R. Meyer, Serial No. 135,037, filed December 24, 1949, entitled Dissolving Metals, now Patent No. 2,649,361. The claims in said parent application relate to alkaline cyanide baths for dissolving metals and particularly to the use of a unique class of activating agents defined therein as consisting of nitro-aromatic materials having potentials greater than -0.90 volt. The claims in this application relate to the use of the same unique class of nitro-aromatic compounds in aqueous acid solutions employed in dissolving metals.

In said parent application, reference is made to several

compounds, to their potentials, and to their effectiveness in accelerating the stripping of nickel when employed in certain concentrations in solutions, as summarized in Table I.

TABLE I

Compound	Voltage	Inches/hr.	G./l.
m HO ₂ SC ₆ H ₄ NO ₂	-0.65	0.002420	57
m HO ₂ CC ₆ H ₄ NO ₂	-0.66		52
m HOCC ₆ H ₄ NO ₂	-0.70	0.000620	38
m H ₂ NC ₆ H ₄ NO ₂	-0.73	0.000598	sat.
1,3 OH-C ₆ H ₃ -2-NO ₂	-0.76	0.000320	39
1,3 OH-2,4,6-NO ₂ -C ₆ H ₃	-0.76	0.000235	21
1,3 OH-2,4-NO ₂ -C ₆ H ₃	-0.78	0.000182	25
p H ₂ NC ₆ H ₄ NO ₂	-0.81	0.000180	sat.
o HO-C ₆ H ₄ NO ₂	-0.83	0.000140	35
o H ₂ NC ₆ H ₄ NO ₂	-0.82	0.000130	sat.

As explained in the parent application, the unique class of nitro-substituted aromatic compounds consists of those nitro-substituted aromatic compounds which, in solution in water, produce an electromotive force of -0.90 volt or a higher voltage than this between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: the temperature is 80° plus or minus 1° C.; the pH is between 8 and 13; the sodium cyanide concentration is approximately 2 molar; and the concentration of a nitro-compound is its saturation value or is about 0.25 gram-mols per liter of the solution, whichever is the smaller.

For example, a test solution saturated with orthonitrochlorobenzene produces, under such conditions, a voltage of minus 0.90 volt. A solution of about 48 g. per liter (0.25 m) of the sodium salt of metanitrobenzoic acid produces, under the prescribed conditions a voltage of about -0.66 volt, that is, a voltage higher than the -0.90 volt of the orthonitrochlorobenzene. Wherever, hereinafter, a voltage producible by a nitro-compound is referred to, it is understood to be a voltage producible between the sheet-nickel electrode and a saturated potassium chloride calomel electrode, under the foregoing conditions.

According to the present invention, improved results are achieved by dissolving metals and/or surface impurities on metals in an acid containing a nitro-aromatic material having a potential, as determined above, greater than -0.90 volt. The range of potentials normally encountered in the nitro-aromatic materials used according to the present invention is approximately between -0.50 and -0.90 volt.

It is an object of the present invention to rapidly dissolve metals in aqueous acid solutions. Certain embodiments of the invention achieve additional advantages. Thus, it is sometimes an object to strip nickel-plating from metals such as copper. It is sometimes an object of the invention to pickle alloys comprising nickel, chromium and/or iron, such as stainless steel and Inconel satisfactorily in order to remove all of the scale without significant corrosion of the acid-resistant alloy. It is sometimes an object of the present invention to provide a method of rapidly dissolving lead from substrate metals such as copper or other metals lower than hydrogen in the electromotive series of metals. It is sometimes an object of the present invention to selectively dissolve metals higher than hydrogen in the electromotive series (e. g., aluminum, zinc, cadmium, lead, nickel, and iron) of metals from the metals lower than hydrogen in the electromotive series of metals (e. g., copper, silver and gold).

Some of the features of the present invention include the use of a member of a unique class of nitro-aromatic compounds as activators for aqueous acid solutions, the rapid dissolving of metals, the achievement of high efficiency in terms of quantities of metals dissolved per stoichiometric unit of acid used, the dissolving of large amounts of metal relative to the consumption of organic modifying agent employed, the absence of insolubilizing residues, the absence of troublesome fumes, the advantageous stability of solution, and the advantageous reproducibility of the reaction. Some of the features of certain embodiments of the present invention include the provision of processes for pickling acid-resistant alloys,

and the provision of a process for dissolving active metals from alloys.

The process of the present invention consists of subjecting a metal to an aqueous acid solution characterized by an organic modifying agent consisting of a nitro-aromatic material having a potential between -0.50 and -0.90 volt. The acid may consist of a strong acid, that is, selected from the class consisting of sulfuric acid, hydrochloric acid, sulfamic acid, hydrofluoroboric acid, and hydrofluosilicic acid, all of which have an ionization constant greater than 0.05 . The acid should be chosen so that it does not form an insoluble film on the metal being dissolved. For example, the lead sulfate film which forms on lead immersed in sulfuric acid makes sulfuric acid unsuited for dissolving lead. Sulfamic, hydrofluosilicic and hydrofluoroboric acids are appropriate in dissolving lead. However, any of the acids are suitable in dissolving aluminum.

The organic modifying agent may be any one of those set forth in the parent application as within the required potential range or other compounds coming within the required potential range and having a significant solubility in the strong acid solution. The concentration of the organic modifying agent should be from approximately 1 gram per liter of the aqueous acid solution to the saturation value of the compound in the strong acid employed for dissolving the metal.

One of the earliest industrial processes for making an organic chemical involved in the reduction of nitrobenzene to aniline by iron and an acid, and it was established that two acid hydrogens were required per nitro oxygen. This two to one stoichiometric ratio of acid hydrogen to nitro oxygen is quite distinguishable from the requirements of the present invention, in which the ratio of acid hydrogen to nitro oxygen, is maintained as high as 300 to one and desirably about thirty to one and never less than three to one. During the operation of the process, additional quantities of acid are added periodically to replace the rapidly consumed acid, and much smaller molar amounts of nitro-aromatic material are added to replace the slowly consumed accelerator. Under ordinary conditions, the concentration of the organic modifying agent will be between 10 and 50% of the weight of the acid employed, but the ratio of nitro oxygen to acid hydrogen (from 3:1 to 300:1 and desirably about 30:1) is more pertinent than the percentage by weight of the reactants.

Under some conditions, competitive reactions permit the metal to be dissolved either by the destruction of the acid hydrogen or by the destruction of the nitro oxygen. When the nitro-aromatic compound is present in a very high concentration, as for example when zinc is treated with a solution containing only water and meta nitrobenzenesulfonic acid, the nitro oxygen readily participates as a reactant to form meta aminobenzenesulfonic acid. According to the present invention, however, the nitro compound functions, not as the principal reactant, but as a catalyst accelerating the reaction between the metal and hydrogen ion. Thus the use of aqueous solutions containing only meta nitrosulfonic acid or mixtures providing an acid hydrogen to nitro oxygen ratio less than three to one are outside the scope of the present invention.

The examples given are only for purposes of illustration and do not limit the invention. Only a few of various modifications of the invention are described in detail in the examples.

EXAMPLE 1

Control not utilizing invention

A solution was prepared consisting of water and 10% sulfuric acid. This aqueous acid solution was heated to 185°F . and employed for dissolving nickel from a nickel-plated copper article. It was found that under these reaction conditions, the nickel was stripped from the copper at a rate corresponding to 0.00002 inch per hour.

EXAMPLE 2

An aqueous acid solution containing 10% sulfuric acid, as in Example 1, was modified by the addition of 10 grams per liter of the sodium salt meta nitrobenzenesulfonate, providing a ratio of 23 atoms of acid hydrogen per atom of nitro oxygen. It was found that at 185°F . the same kind of nickel-plated copper employed in Example 1 could be stripped at a rate corresponding to

0.002 inch per hour, thus indicating that there was a one hundredfold increase in the activity of the acid by this small concentration of the organic modifying agent. As previously noted, sodium meta nitrobenzenesulfonate has a potential of -0.65 volt. In the acid solution, the salt was converted to the acid. Hence meta nitrobenzenesulfonic acid can be employed directly when desired.

By the use of 25 grams per liter of the meta nitrobenzenesulfonate, providing an acid hydrogen to nitro oxygen ratio of about 10 to 1, the same type of nickel-plated copper was stripped at 185°F . to remove nickel at the rate of 0.004 inch per hour or double the reaction rate obtained by using only 10 g. per liter.

EXAMPLE 3

A series of tests was conducted to determine the effects of temperature upon the rate of dissolving the metal. A solution was prepared containing approximately 10% sulfuric acid and 10 grams per liter of sodium meta nitrobenzenesulfonate. When a special type of nickel-plated copper was subjected to the solution at 100°F . the rate of dissolving was 0.002 inch per hour. At 140°F . the rate was 0.003 inch per hour. At 160°F . it was 0.005 inch per hour and at 180°F . it was 0.008 inch per hour. On the bases of tests such as these, it was established that the reaction should be conducted at a temperature between 70°F . and the boiling point of the aqueous acid solution, preferably about 180°F .

EXAMPLE 4

A solution of 10% sulfuric acid was heated to 180°F . and modified by the addition of 25 grams per liter of meta nitroaniline, which has a potential of -0.73 volt. It was found that the nickel was stripped from the nickel-plated copper at a rate of 0.0043 inch per hour.

EXAMPLE 5

An aqueous acid solution consisting essentially of 10% sulfuric acid was modified by the addition of 25 grams of para nitroaniline, which has a potential of -0.81 volt. Such proportions provided an acid hydrogen to nitro oxygen ratio of about 6 to 1. It was found that this solution was capable of dissolving nickel from nickel-plated copper at a rate of 0.0052 inch per hour at 180°F . Thus the reaction rate was about 21% greater than in Example 4 by reason of the more effective catalyst.

EXAMPLE 6

A mixture of copper and lead was placed in a polyethylene beaker and treated with hydrofluoroboric acid in a concentration of 15%. Then the acid was modified by the addition of 25 grams per liter of para nitroaniline providing an acid hydrogen to nitro oxygen ratio of about 5 to 1. The effectiveness of the modifying agent in accelerating the dissolving of the lead was quite conspicuous. Sulfamic acid, fluosilicic acid and fluoroboric acid can be used in dissolving lead according to the present invention.

EXAMPLE 7

A solution containing 200 grams per liter of sulfuric acid and 5 grams per liter of meta nitrobenzenesulfonic acid was tested and found to have substantially no action upon a nickel-plated sheet of copper at room temperature. However, by heating the acid solution up to a temperature of approximately 185°F ., the nickel was rapidly stripped from the copper. It was found that there was a threshold temperature of about 120°F . below which the nickel was not corroded or dissolved at any significant rate, whereas, above that temperature, the nickel was stripped rather rapidly.

EXAMPLE 8

In an industrial manufacturing process, bundles of stainless steel tubing (type 316 alloy) were regularly subjected to a heat treatment process whereby a significant amount of scale was formed both on the interior and exterior of the tubes. It was essential that all scale be removed both from the exterior and interior of the tubes, because they were scheduled for passage through a series of dies, in which any residual scale impaired the effectiveness of the die lubricant. By subjecting the tubes to a seven-step operation employing sodium hydride as the principal reagent, and by then repeating the seven steps, that is, by a fourteen step de-scaling operation, the tubes were satisfactorily cleaned. Tests were conducted which

demonstrated that the tubes could not be adequately cleaned by 30% sulfuric acid at 200° F. nor by immersion for thirty minutes in a mixture of 10% nitric and 4% hydrofluoric acids at 130° C., nor by 22% nitric acid at 110° C., nor by a mixture of 25% chromic acid and 30% sulfuric acid at 200° F. nor by numerous other relatively powerful pickling solutions.

A solution was prepared consisting of 200 g./l. of sulfuric acid, and 40 g./l. of meta nitrobenzenesulfonic acid and 16 g./l. of hydrofluoric acid. This solution was heated to 150° and proved to be a highly efficient pickling solution for the difficultly cleaned stainless steel tubes. Thus a process requiring only a single treating bath, characterized by the accelerator of the present invention, and a rinsing operation removed the scale from the stainless steel more effectively than the fourteen step industrial procedure which it replaced. Moreover, the stainless steel pickling operation of the present invention involves no troublesome fumes, adherent residues, or related difficulties. Although described in connection with stainless steel type 316 alloy, the invention is applicable to several other acid-resistant alloys. For example, an Inconel alloy containing approximately 14% chromium, 80% nickel, and 6% iron was satisfactorily treated by this pickling method. Other alloys comprising at least two components from the class consisting of iron, nickel and chromium were also treated with this solution to remove scale rapidly without significant pitting or corrosion of the underlying alloy.

EXAMPLE 9

A stainless steel sheet having mill scale might be subjected to a solution containing 200 g./l. of sulfuric acid and 30 g./l. of meta nitrobenzenesulfonic acid at 185° F. to satisfactorily pickle it without significant corrosion of the sheet.

EXAMPLE 10

A brass article might be immersed in a hot solution of 10% sulfuric acid containing 60 g./l. of sodium meta nitrosulfonate in order to prepare a porous copper article. The control of the oxidizing activity of the solution by means of the nitro organo accelerator would make possible the rapid dissolving of the zinc from the brass without disintegration of the copper framework of the alloy.

EXAMPLE 11

A solution of 15% sulfuric acid might be saturated with nitrophthalic acid and employed to strip nickel from copper articles at an accelerated rate. Mixtures of nitrophthalic acid and nitrobenzenesulfonic acid would also be effective accelerators.

EXAMPLE 12

Nickel plated copper articles might be stripped at an accelerated rate by treatment with a solution of 20% hydrochloric acid containing 30 g./l. of para nitroaniline at 150° F.

There are other chemicals which are within the scope of the unique class of nitro-aromatic materials. Particular advantages have been established for the use of compounds chosen from the class consisting of nitrophthalic acid, nitrobenzenesulfonic acid, nitroaniline and mixtures thereof.

The use of the unique class of nitro-aromatic materials, although of value in any application of the treatment of metals with acids, has particular industrial significance in the pickling of alloys normally resistant to acids, said alloys consisting principally of two or more metals chosen from the class consisting of chromium, iron and nickel.

The several examples set forth merely illustrate some of the applications of the use of the unique class of nitro-aromatic materials as accelerators to increase the reaction rate of an aqueous acid solution in contact with impurities on a metal surface or a metal higher than hydrogen in the electromotive series of metals.

The invention claimed is as follows:

1. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous strong acid solution containing a nitro-aromatic compound having a potential greater than -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: tem-

perature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller.

2. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous strong acid solution having an ionization constant greater than 0.05 containing a nitro-aromatic compound having a potential between -0.50 and -0.90 volt as measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller.

3. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous acid solution containing an acid having an ionization constant greater than 0.05 and in a concentration of at least 1% and not more than 50% and a nitro-aromatic material having a potential between minus 0.50 and minus 0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, in a concentration of at least 0.1% and not more than 25%.

4. A metal-dissolving solution consisting of water, a strong acid in a concentration from 1% to 50%, and a nitro-aromatic material in a concentration from 0.1% to 25%, said nitro-aromatic material having a potential between minus 0.50 and minus 0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller.

5. A concentrate adapted for the preparation of an acid-dissolving solution consisting essentially of a concentrated strong acid having an ionization constant greater than 0.05 and a nitro-aromatic material having a potential between minus 0.50 and minus 0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, the concentration of the nitro-aromatic material being from 1 to 25% of the composition.

6. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous strong acid solution containing a nitro-aromatic material chosen from the group consisting of nitrophthalic acid, nitrobenzenesulfonic acid, and nitroaniline.

7. The process which includes the step of treating a metal with an aqueous acid solution containing nitrobenzenesulfonic acid.

8. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous strong acid solution containing a nitrophthalic acid.

9. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous strong acid solution containing a nitroaniline.

10. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of treating the metal with an aqueous acid solution containing an acid having an ionization constant greater than 0.05 in a concentration of at least 1% and not more than 50%, and a nitro-aromatic material having a potential between minus 0.50 and minus 0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following

conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, in a concentration of at least 0.1% and not more than 25% and a temperature between 70° and 212° F.

11. The process of claim 10 in which the temperature of the treatment of the metal is approximately 185° F.

12. The process of dissolving metals higher than hydrogen in the electromotive series of metals which includes the step of preparing a solution consisting of water, an acid having an ionization constant greater than 0.05 in a concentration of at least 1% and not greater than 50% and a nitro-aromatic material having a potential between -0.50 and -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, in a concentration of at least 1 gram per liter and not greater than the saturation value of the nitro-aromatic material at the temperature employed, heating said solution to a temperature in excess of 140° F., subjecting the metal to the aqueous acid solution at the elevated temperature whereby the acid is dissolved at a rate accelerated by the presence of the nitro-aromatic compound, continuing the treatment of the metal with the acid, and replenishing the acid and nitro-aromatic compound periodically.

13. The process of pickling alloys containing two or more metals from the class of chromium, iron and nickel which includes the step of treating alloy having mill scale thereon with a hot aqueous acid solution containing a strong acid having an ionization constant greater than 0.05, and containing a smaller amount of nitro-aromatic compound having a potential between -0.5 and -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, whereby the mill scale is dissolved from the alloy without corrosion or rapid dissolving of the body thereof.

14. The process of claim 13 in which the acid solution contains hydrofluoric acid in a molar concentration greater than that of the nitro-compound but less than that of the strong acid, and in which the nitro-aromatic compound is chosen from the class consisting of nitrophthalic acid, nitrobenzenesulfonic acid and nitroaniline.

15. The process of dissolving lead which includes the treatment of lead with an aqueous acid solution containing an acid chosen from the class consisting of hydrofluoroboric, hydrofluosilicic and sulfamic acid, and a nitro-aromatic compound having a potential between -0.50 and -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, in a concentration of from 0.1% to 25%.

16. The process of preparing porous copper which consists of treating an alloy consisting of copper and zinc with an aqueous acid solution characterized by a strong acid having an ionization constant greater than 0.05 and a nitro-aromatic material having a potential between -0.50 and -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, whereby the zinc is dissolved from the alloy, leaving a porous copper structure unaffected by the acid.

17. The process of treating metals with acid which consists of preparing an aqueous solution containing a strong acid having an ionization constant greater than 0.05, in a concentration between 1 and 50%, adding a nitro-aromatic material having a potential between -0.50 and -0.90 volt measured between a sheet-nickel electrode and a saturated potassium chloride calomel electrode under the following conditions: temperature 80° plus or minus 1° C.; pH between 8 and 13; sodium cyanide concentration approximately 2 molar and the concentration of the nitro-compound at its saturation value or about 0.25 gram-mol per liter of solution, whichever is the smaller, in an amount sufficient to provide a ratio of acid hydrogen to nitro oxygen of at least 3 to 1, heating said solution, subjecting the metal to the hot solution, and replenishing the acid and nitro compound to maintain said acid hydrogen to nitro oxygen ratio.

18. The process of claim 17 in which the acid hydrogen to nitro oxygen is maintained at about 10 to 1.

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