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3,367,874

PROCESS AND COMPOSITION FOR ACID
DISSOLUTION OF METALS

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No Drawing. Continuation-in-part of application Ser. No. 450,211, Apr. 22, 1965. This application Sept. 23, 1966, Ser. No. 581,437

5 Claims. (Cl. 252—79.2)

This is a continuation-in-part application of copending application Ser. No. 450,211, filed Apr. 22, 1965, now abandoned, entitled Dissolution Process, by the inventors herein.

This invention relates to a process of acid dissolution of metals, and more particularly to special additives for nitric acid dissolution baths to be used on metals such as nickel, copper, zinc, cobalt and iron.

Many industrial processes involve acid treatment of metals during which metal dissolution occurs. Some of the more important of these are (1) acid stripping of plating racks, (2) pickling, and (3) chemical metal salt manufacture.

The invention herein was conceived because of the problems encountered with stripping of plating racks, and thus will largely be explained with respect thereto. It will be apparent, however, upon studying the concept presented, that the invention can be employed in other metal dissolution processes. It therefore should not be strictly limited to rack stripping.

Stripping of the plate off the plating racks is conventionally necessary after plating articles suspended on the racks, since the racks are also metallic and electrically conductive. Consequently, they are plated as well as the suspended articles. This stripping is largely done by vigorously manually pounding these racks. This constitutes hard labor for the workmen, and further requires considerable labor time. It is very costly.

Instead of manual or mechanical methods, some attempts have been made at acid dissolution. The racks are then made of stainless steel, which is acid resistant, so that the plated material can be dissolved off by acid to enable re-use thereof. Concentrated commercial nitric acid, i.e. about 68% nitric acid in aqueous solution, can be employed to dissolve the plated metal which may be nickel, copper, zinc, cobalt or the like. The chemical reaction of the concentrated nitric acid bath works fairly effectively, once the reaction has proceeded for a considerable time. However, the reaction normally starts very slowly. It proceeds somewhat more rapidly if heated. Even so, however, after the process is started and finally proceeding smoothly, it still requires a considerable time period to dissolve the metal plate. Because of these significant difficulties encountered with attempted acid dissolution, resort is usually made to the old mechanical methods of stripping, particularly pounding.

The inventors herein sought a unique way to significantly accelerate the dissolution process of concentrated nitric acid baths. Particularly, it was intended to improve concentrated nitric acid baths so that (1) the initial reaction started practically instantly rather than with a delay characteristic common to present baths, and (2) the total reaction rate would be much faster.

It is an object of this invention to provide special additives for a nitric acid metal dissolution bath, that results in a quickly initiated reaction, and an increase of chemical reaction rate many times normal.

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Another object of this invention is to provide a nitric acid bath having a rapid initial dissolution reaction on metals such as nickel, copper, alloys of copper, zinc, cobalt, and iron, and also causing a total dissolution process time much shorter than conventionally required. The bath has no significant effect on stainless steel, so that it is extremely useful for processes such as rack stripping. It also substantially prevents the formation and ebullition of noxious fumes even though containing only a small inexpensive amount of special additive.

These and several other objects will become apparent upon studying the following specification.

As noted previously, in plating processes, metals such as nickel, copper, cobalt, zinc, and others not only plate on the articles suspended on racks in the plating baths, but also plate on the racks themselves. These racks are made of metal, usually stainless steel, to have capacity to conduct electrical current from a common bus bar to the articles. After a period of usage, the metal coating on the racks becomes very substantial and must be removed. If the racks are immersed in a conventional concentrated nitric acid bath, the dissolution process is relatively slow, particularly at the outset of the reaction. During the process, noxious fumes are driven off in substantial volumes, particularly deadly nitrogen dioxide.

Similar conditions occur during pickling operations, and other processes where metal such as iron, copper, copper alloys such as those of bronze and brass, nickel, etc. are dissolved.

The inventors herein discovered a nitric acid bath composition that is many times faster in its reaction rate on metals than the conventional bath. They discovered that the novel bath causes a process which begins reaction immediately and rapidly, and proceeds at a rate many times greater than normal, yet remains completely under control.

Since the conventional nitric acid bath dissolution processes are accompanied by the evolution and ebullition of considerable quantities of nitrogen dioxide fumes, it might be logically assumed that the tremendous increase in the rate of reaction of the novel bath would be accompanied by an almost violent emission of potent gases. However, the novel bath, even though increasing the rate of reaction many times, is characterized by the fact that the ebullition of oxides of nitrogen is substantially prevented. Comparative tests show that during reaction the bath shows no yellowish or brownish discoloration as normally occurs.

It will be realized that such results are of tremendous significance in metal dissolution processes, particularly industrial processes where large vats of acid are employed to receive large items in batch fashion, or where vats receive large quantities of items per unit of time on a continuous basis.

These results would be worth a substantial increase in initial bath cost. Yet, with the invention, these results can be achieved by the addition of a small amount of relatively inexpensive additive, so that the added cost is actually very small.

The novel bath is preferably formed with the use of concentrated nitric acid, the term "concentrated nitric acid" being intended to encompass the variations found in commercial concentrated nitric acid. It is usually about 68% by weight acid in an aqueous solution, with a specific gravity of about 1.42. Regular "technical grade" nitric acid can be employed. This particular percentage can vary somewhat without departing from the concept

presented herein. That is, improved results will also occur with greater water content in the nitric acid baths, but the best results for practical operations occur at the higher concentrations of acid.

Subsequent to the applicant's initial work described in the parent application above, considerable subsequent testing and experimentation has shown that particular additives have a markedly better action on the nitric acid bath dissolution process.

The accelerating agents which were discovered to be particularly effective can be grouped into the following categories:

- (I) compounds capable of forming a sulfamate anion in solution and not forming undesirable side reactions or precipitates, namely amino sulfonic acids and metal salts thereof set forth in detail hereinafter; and
- (II) the combination of urea and sulfamic acid, which in solution is frequently termed urea sulfamate, i.e. in compound form, or in the form of certain compounds to be named hereinafter capable of forming an urea cation and a sulfamate anion in solution.

GROUP I

Examples of group one compounds capable of forming the sulfamate anion in solution without other undesirable reactions occurring are the amino sulfonic acids and salts thereof, namely:

- (a) sulfamic acid and sulfamate salts of ammonium, sodium, potassium, ammonium, copper, nickel and iron;
- (b) amine disulfonic acid and its salts of sodium ammonium and potassium;
- (c) amine trisulfonic acid and its salts of ammonium and potassium.

GROUP II

The most effective accelerating additive is one containing a mixture of urea and sulfamic acid. The simplest form of this is the direct compound, urea sulfamate. However, this compound is not too readily available commercially, and can be formed in situ in the bath by adding a mixture of components that will form the needed urea ions and sulfamate ions. The sulfamate ion-producing component must be one which will not cause undesired side effects, and therefore should be one of those named in Group I above. Also, although it is simplest to simply add urea itself, any of the following urea compounds may be added to the ones in Group I to obtain the necessary mixture, namely urea acid salts of urea nitrate, urea phosphate, urea sulfate, and urea hydrochloride, and the related compound guanilylurea sulfate.

Extensive experimentation has been conducted to test these compounds and many many others after the initial discovery was made.

The continued experimentation has now shown that baths containing the two designated groups of compounds are markedly superior to conventional nitric acid baths and to baths containing just urea compounds. The chart below is representative of the superior results obtained. These materials were run under essentially identical conditions for close comparison. Specifically the bath volumes and temperatures were the same, and the metal pieces were of the same weight, size and surface area. In the illustrative chart below, the baths were made up by dissolving the appropriate amount of the compound/s under examination to affect the desired concentration in 14 ml. of water. This solution was then stirred into 280 ml. of commercial grade concentrated nitric acid, 42° Be. The bath was brought to 28° C. and a piece of electrolytically deposited nickel, previously weighed, was immersed in the bath for five minutes, the temperature being maintained at 28° C. during that time. The nickel piece was then withdrawn, rinsed and weighed to determine the amount dissolved in the bath. In all cases the

nickel pieces were of the same dimensions to obviate discrepancies due to surface area.

Additive	Additive Concentration, gm./l.		
	1	5	10
Metal Loss (gm. Ni/5 Min., 28° C.)			
None.....	(¹)		
Urea.....	0.1	0.1	0.1
Sulfamic Acid.....	0.1	0.4	² 0.6
Urea + Sulfamic Acid.....	0.3	0.6	² 1.7
Potassium Amine-trisulfonate.....			.5
Potassium Amine-trisulfonate + Urea.....			1.1
Ammonium Amine-disulfonate.....			.9
Ammonium Amine-disulfonate + Urea.....			1.5

¹ Negligible.

² This sulfamic acid was apparently in excess of saturation and precipitated out. In all other baths a clear solution was had.

In the above table where a combination of additives was used, each was at the designated concentration. Thus, in the bath containing urea and sulfamic acid, 1 gm./l. of urea and 1 gm./l. of sulfamic acid were used, etc.

From the above table it is apparent that each of the combinations is better with respect to dissolution rate than the sum of each of the separate compounds.

In all cases there was no evolution of nitrogen dioxide.

The results of these tests established the fact that a wide range of concentrations are effective.

In general, it has been found by experimentation that the concentration of the additive should be at least about 0.05 gram per liter of acid solution, in order to be significantly effective from a practical standpoint. More than this may be added if desired, to assure a constant supply of at least this concentration. In fact, optimum concentration is normally about 1 to 10 grams per liter, but this varies somewhat with the molecular weight of the additives, and the ratio of the atomic weight of the effective ions to the total molecular weights. Concentrations in excess of saturation can be employed.

In terms of percentages, the preferred bath of urea and sulfamic acid consists essentially of 0.00352% to 10.0% by weight of urea, 0.00352% to 10.0% by weight sulfamic acid, 0% to 20% by weight of water and 60.0% to 99.9936% by weight nitric acid. The additive consists essentially of 5% to 50% by weight of urea, 50% to 5% by weight of sulfamic acid, and the balance water.

The concentration may be maintained at the selected value by periodic additions. Even if the concentration is increased in excess of the saturation point of the additive/s in the nitric acid solution, no detrimental results have been found to occur because of the excess.

With the use of the novel bath, elevated temperatures above normal room temperatures are not really necessary. Neither is it necessary to add hydrochloric acid to the bath.

As indicated previously many experiments were conducted to determine and test the concept taught above, and the specific materials noted in each group. These were all tested and extensive experimental results could be listed. However, since the potential combinations are so many, the resultant listing would necessitate many pages of this application, and would be largely superfluous. The following representative examples are typical of the results.

EXAMPLE I

A stainless steel element coated with copper was immersed in a bath of commercial concentrated nitric acid (about 68% acid in aqueous solution) to which 0.03 gram per liter of urea and 0.02 gram per liter of sulfamic acid were added. Dissolution started immediately (in contrast to prior baths) and proceeded vigorously and smoothly. No nitric oxide fumes were expelled.

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EXAMPLE II

A stainless steel element coated with nickel was immersed in a bath of concentrated nitric acid to which 1.0 gram per liter of sulfamic acid had been added. Dissolution started immediately and proceeded smoothly. No nitric oxide fumes were expelled.

EXAMPLE III

A stainless steel element plated with cobalt was immersed in a concentrated nitric acid bath to which 0.5 gram per liter of urea and 0.5 gram per liter of sodium sulfamate had been added. Dissolution started immediately and proceeded smoothly and vigorously. No nitric oxide fumes being expelled.

EXAMPLE IV

An article with an external layer of zinc was immersed in a concentrated nitric acid bath to which 0.06 gram per liter of urea and 0.02 gram per liter of potassium amine disulfonate had been added. Dissolution started immediately and proceeded rapidly. No nitric oxide fumes were expelled.

EXAMPLE V

An iron article was immersed in a concentrated nitric acid bath to which 0.04 gram per liter of urea sulfate and 0.02 gram per liter of amine trisulfonic acid were added. Dissolution proceeded rapidly and vigorously, with no noxious oxides of nitrogen being expelled.

Other representative specific experiments are the following additives in the noted amounts added to a concentrated nitric acid bath and used to dissolve the noted metal, with the advantageous results above occurring:

Additive	Amount (g./l.)	Metal
1. Sodium sulfamate	0.06	Ni
2. Ammonium sulfamate	0.10	Cu
3. Copper sulfamate	0.12	Zn
4. Nickel sulfamate	0.08	Co
5. Iron sulfamate	0.13	Fe
6. Sodium amine disulfonate	0.20	Co
7. Potassium amine disulfonate	0.07	Zn
8. Potassium amine trisulfonate	0.44	Cu
9. Urea sulfamate	0.29	Ni
10. Urea and sodium sulfamate	0.06+0.06	Ni
11. Urea nitrate and potassium sulfamate	0.09+0.03	Zn
12. Urea phosphate and ammonium sulfamate	0.13+0.12	Co
13. Urea sulfate and copper sulfamate	0.14+0.08	Ni
14. Urea hydro-chloride and nickel sulfamate	0.20+0.09	Fe
15. Urea nitrate and sodium amine disulfonate	0.11+0.10	Co

As noted previously, it is believed that dozens of more examples which could be given would really be superfluous. Those noted serve to show specific applications of the teachings, to enable one having ordinary skill in the art to practice the concept presented.

It is conceivable that certain additional minor additives could be added to the bath for other reasons if desired. It is also conceivable that the temperature of the bath could be controlled to even further regulate the rate of reaction. These modifications could be done without altering the basic concept of the invention, provided the specific additives noted are present in at least the minimum practical concentration noted. The invention is in-

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tended to be limited only by the scope of the appended claims and the reasonable equivalents to those defined therein.

We claim:

1. A metal dissolving nitric acid bath for dissolving metals selected from the group consisting of nickel, copper, zinc, cobalt, and iron, consisting essentially of at least about 0.05 gram per liter and up to saturation of an additive consisting essentially of: a mixture of substances capable of providing urea in the bath and capable of forming sulfamate ions in the bath, said substance capable of providing sulfamate ions in the bath being selected from the group consisting of sulfamic acid, amine disulfonic acid, amine trisulfonic acid, and salts thereof, and said substance capable of providing urea in the bath being selected from the group consisting of: urea; urea nitrate; urea phosphate; urea sulfate; urea hydro-chloride; guanylurea sulfate; and urea sulfamate.

2. The bath in claim 1 wherein said additive is urea sulfamate.

3. A metal dissolving bath consisting essentially of 0.00352% to 10.0% by weight of urea, 0.00352% to 10% by weight of sulfamic acid, 0% to 20% by weight of water, and 60% to 99.9936% by weight of nitric acid.

4. A method of rapidly dissolving a metal from the group consisting of nickel, copper, zinc, cobalt, and iron comprising the steps of: providing a nitric acid bath; adding to said bath at least 0.05 gram per liter of and up to saturation of an additive consisting essentially of: a mixture of substances capable of providing urea in the bath and capable of forming sulfamate ions in the bath, substance capable of providing sulfamate ions in the bath being selected from the group consisting of sulfamic acid, amino disulfonic acid, amino trisulfonic acid, and salts thereof, and said substance capable of providing urea in the bath being selected from the group consisting of: urea; urea nitrate; urea phosphate; urea sulfate; urea hydro-chloride; guanylurea sulfate; and urea sulfamate; and immersing the metal in said bath.

5. A method of rapidly dissolving a metal from the group consisting of nickel, copper, zinc, cobalt, and iron comprising the steps of: providing a nitric acid bath consisting essentially of 0.00352% to 10% by weight of urea, 0.00352% to 10% by weight of sulfamic acid, 0% to 20% by weight of water, and 60% to 99.9936% by weight of nitric acid; and immersing the metal in said bath.

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