

UNITED STATES PATENT OFFICE

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STAINLESS STEEL PICKLING BATH SOLUTION

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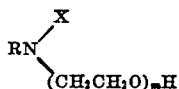
No Drawing. Application August 16, 1949, Serial No. 110,673

11 Claims. (Cl. 252-101)

1 This invention relates to pickling baths for stainless steel having a surface film of metal oxide.

In the production of stainless steel wire, sheets, and strips, a clean bright finish is produced by pickling in a bath of nitric acid containing hydrofluoric acid. The pickling operation may be carried out either batchwise or continuously and is most conveniently carried out on wire and strips by passing them continuously through the pickling bath. Since the continuous process is subject to fairly exact control and is, therefore, amenable to rapid pickling, means for accelerating the pickling action of the acids in the pickling bath are highly desirable.

In accordance with the present invention, it has been found that stainless steel pickling bath solutions containing nitric acid and hydrofluoric acid are accelerated in their pickling action on stainless steel when they contain dissolved therein small amounts of a glycol ether of an ethanol rosin amine having the general formula



where R is a radical of the group consisting of dehydroabietyl and hydroabietyl, X is a radical of the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being within the range of 11 to 40.

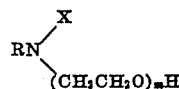
For convenience of expression in this application, these glycol ethers of the ethanol rosin amines of this invention will be referred to generally as "addition agents" and this phraseology will be understood to refer to the addition agents of the present invention when so used.

The following examples are illustrative of the pickling bath solutions of this invention and the manner in which they are used.

Examples 1-7

Rolled stainless steel sheets of the 18-8 type (about 18% chromium and about 8% nickel) as they come from the rolling mill and having an oxide coating were cut into small panels 2 inches long and 1 inch wide and arranged for simultaneous dipping in separate pickling baths. The baths all contained 7% nitric acid, 1% hydro-

2 fluoric acid and about 92% water. Each bath solution contained in addition 0.2% of a glycol ether of an ethanol dehydrogenated rosin amine of the formula



where R is the dehydroabietyl radical and X is a radical of the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. One bath solution was a blank and contained only the nitric acid and hydrofluoric acid.

The panels were weighed, immersed with agitation in the baths (heated at 150-160° F.) for 45 seconds, and withdrawn for observation for 30 seconds. This process was repeated until all panels were free of scale on one side. This required 7 cycles of 75 seconds each. The panels were all weighed for weight loss after 11 cycles when the heavier scale of the second side was completely dissolved.

The addition agent in Examples 1, 3, 5, and 7 were mixtures containing compounds in which X is hydrogen and compounds in which X is $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$. The addition agents in Examples 2, 4, and 6 were made from diethanol dehydrogenated rosin amine and were chiefly diethanol dehydroabietylamine derivatives of the above general formula where X is



only and m and n were substantially equal. The sum of m and n in these addition agents was 12 in Example 1, 10 in Example 2, 18 in Example 3, 20 in Example 4, 28 in Example 5, 30 in Example 6, and 37 in Example 7. All of the addition agents were of the type in which R of the formula is dehydroabietyl.

The pickling as shown by visual observation was complete in Examples 5 and 7 at the end of the fourth cycle, in Examples 3, 4, and 6 at the end of the fifth cycle, in Examples 1 and 2 at the end of the sixth cycle, and in the blank at the end of the seventh cycle. After 11 cycles, both sides of all of the panels were clean. The samples including the blank were weighed and found to have a total weight loss of $2.28\% \pm 0.18\%$, the blank having, within experimental error, no different weight loss from the panels in the pickling

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bath solutions containing addition agents. In all cases the panels pickled in bath solutions containing the addition agents were 95% clean before the blank had become 70% clean.

Example 8

Example 5 was repeated using various concentrations of addition agent in the pickling bath. A noticeable improvement in rate of pickling was noted in solutions containing as small an amount as 0.001% addition agent. Very little difference in rate of pickling was found between the use of 0.2% addition agent and 0.1% addition agent. However, the useful life of the pickling solution was greatly increased by the use of more than 0.2% addition agent and as much as 3% addition agent was found to be operable.

Example 9

An aqueous bath containing 20% nitric acid and 5% hydrofluoric acid and 0.2% of the addition agent of Example 5 was compared with an aqueous bath containing 7% nitric acid, 1% hydrofluoric acid, and 0.2% of the same addition agent and the corresponding blanks without the addition agent for stability. In this test the baths were each first heated at 154° F. for 7 hours and were then tested for their relative speed of removal of the oxide film from stainless steel panels at 150–160° F. The baths containing the addition agents were still more active than the blanks in removing the oxide coating after this aging treatment. A similar comparison showed the other addition agents of this invention to have sufficient stability to maintain their effectiveness in these pickling solutions containing both nitric and hydrofluoric acids.

The addition agents used in accordance with this invention are surprisingly stable in the nitric acid solutions containing hydrofluoric acid. The stability appears to be dependent upon the presence of hydrofluoric acid in the solution and at least about 1% hydrofluoric acid must be present for continued stability. The stability of the addition agents also decreases with increasing nitric acid content, but is commercially satisfactory in solutions containing as high as 20% nitric acid when at least 1% hydrofluoric acid is present. The commercially satisfactory pickling baths containing addition agents of this invention will contain about 5 to 20% nitric acid and about 1 to about 5% hydrofluoric acid along with the addition agents.

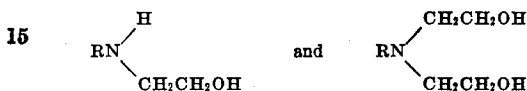
The amount of addition agent may be from about 0.001% to about 3% based on the weight of the pickling bath. The preferred range is 0.05 to about 0.5% addition agent.

The pickling baths of this invention are useful for pickling corrosion-resistant irons and steels commonly referred to as "stainless" irons and steels, i. e., alloys of iron and chromium with or without other elements such as carbon, nickel, manganese, titanium, etc. It is particularly well suited for those stainless steels and irons which are worked into sheets, strips, and wires which can be pickled continuously. These baths are more suited for the more highly corrosion-resistant irons and steels containing at least 7% chromium and is particularly suited for alloys containing up to about 30% chromium along with nickel. The addition agents of this invention are thus useful in conjunction with any nitric acid-hydrofluoric acid pickling baths which are used on iron-chromium alloys commonly referred to as corrosion-resistant or stainless irons and

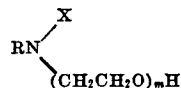
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steels. The pickling baths containing the addition agents of this invention are particularly useful for producing a bright finish on stainless steel surfaces because they prevent any tendency of the pickling bath to cause staining of the stainless steel such as is frequently caused by organic substances added to pickling baths containing nitric acid.

The glycol ethers of ethanol rosin amines of this invention are produced by reacting a hydrogenated or dehydrogenated rosin amine with ethylene oxide. The initial product is believed to be ethanol rosin amines having the formulas



where R is the organic radical of the rosin amine, i. e., dehydroabietyl or hydroabietyl. The products of this invention are the products of further reaction with ethylene oxide in which the alcohol groups of the initial product react with the formation of ether linkages. Thus, the product of reaction of rosin amine with 40 moles of ethylene oxide is a substance of the general formula



where X is a radical selected from the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ where m is an integer from 10 to 40 and n is an integer from 1 to 30 and the sum of m and n falls within the range of 11 to 40. The product may contain both the glycol ether of monoethanol rosin amine and the glycol ether of diethanol rosin amine, the total number of $-(\text{CH}_2\text{CH}_2\text{O})$ -units being equal to the number of moles of ethylene oxide added whether such units are attached to the nitrogen as a single chain or as two chains. The composition will depend somewhat upon the method of preparation. In these formulas where R is the organic radical of a rosin amine, it is intended that the radical shall include the dihydroabietyl radical, the tetrahydroabietyl radical and the dehydroabietyl radical.

The reaction of rosin amine with ethylene oxide for the production of the addition agents of this invention is generally carried out by heating rosin amine with 1% of its weight of sodium methoxide to about 150° C. and adding the desired weight of ethylene oxide gas gradually until the desired absorption is obtained. Products prepared in this manner contain a high percentage of glycol ethers of the type in which one hydrogen remains on the nitrogen and the $-(\text{CH}_2\text{CH}_2\text{O})$ -units are attached to the nitrogen as a single chain. Apparently, the alcoholic hydrogens are more reactive toward ethylene oxide in the presence of a catalyst than are the hydrogens attached to the nitrogen of the partially substituted rosin amines. By this method of preparation, there is thus a tendency toward products having $-(\text{CH}_2\text{CH}_2\text{O})$ -chains of different lengths or having only one such chain. It is, therefore, understood that the products of this invention prepared in this manner are generally mixtures and the value of m in the formulas used in the specification and claims is indicative of average analyses rather than any chemical individual.

The glycol ethers of diethanol rosin amines of this invention which have two glycol ether chains may be prepared free of glycol ethers of monoethanol rosin amines by reacting a rosin amine

with ethylene oxide in the absence of a catalyst to produce as an initial product diethanol rosin amine, and subsequently adding a catalyst and continuing the reaction of the diethanol rosin amine with ethylene oxide. The first reaction in the absence of the catalyst is preferably carried out in alcoholic solution at atmospheric pressure and the second reaction in the presence of a catalyst is carried out in the absence of alcoholic solvent. The usual catalyst for the condensation of ethylene oxide with alcoholic hydroxyls include sodium hydroxide and sodium alkoxides such as the methoxide, ethoxide, propoxide, etc., and the corresponding potassium compounds.

The glycol ethers of the ethanol rosin amines should be substantially free of compounds containing the abietyl nucleus, i. e., less than about 5% of glycol ethers of ethanol abietylamine or abietylamine itself since the pickling baths of the nitric acid content of this invention require an addition agent which has a relatively high degree of stability against oxidation.

The rosin amines from which the glycol ethers of the ethanol rosin amines of this invention are prepared are the rosin amines which are prepared by reacting ammonia with a modified rosin such as hydrogenated rosin or dehydrogenated rosin to form the nitrile from the carboxyl group in the rosin and then hydrogenating the modified rosin nitrile to form the amine. The preparation of the nitrile may be carried out by passing gaseous ammonia into the molten rosin material and vaporizing the water as fast as it is formed in order to remove the water from the reaction mixture. Dehydration catalysts may be used to facilitate the reaction with ammonia, if desired. The nitrile is preferably purified by neutralization or distillation to make it suitable for hydrogenation to the amine as the presence of acidic materials frequently destroys the hydrogenation catalyst. The nitrile may be formed from any modified rosin containing chiefly hydrogenated rosin or dehydrogenated rosin. The nitrile used should preferably contain less than about 10% abietonitrile. The rosin nitriles may likewise be made from the rosin acids which are major constituents of these rosins such as dihydroabietic acid, dehydroabietic acid, and tetrahydroabietic acid.

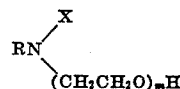
The resin acid nitriles prepared from the modified rosins or the corresponding rosin acids are readily hydrogenated to the amines. The hydrogenation is usually carried out by heating the rosin nitrile at about 150° to 200° C. with a Raney nickel catalyst under hydrogen pressure up to about 8000 lb./sq. in. The hydrogenation may also be carried out using other catalysts such as Raney cobalt, supported nickel or cobalt catalysts and noble metal catalysts such as platinum, palladium, palladium on carbon, or reduced platinum oxide. The reaction may be carried out under hydrogen pressure of from about 200 to 8000 lb./sq. in. and at a temperature of from about 20° C. to about 200° C. Solvents may be used if desired and are preferable at the lower temperatures. The hydrogenation may also be carried out in the presence or absence of ammonia. Although the hydrogenation is ordinarily carried out only to the extent of hydrogenation of the nitrile group which hydrogenates quite readily, the hydrogenation may also be carried out under such conditions of temperature, pressure, and time of hydrogenation as to hydrogenate the rosin amines which are produced to convert them to hydrosin amines which corre-

spond to the amines produced from hydrogenated rosin via the nitriles.

For convenience of expression in this specification, the hydroabietyl, and dehydroabietyl radicals are referred to with the intention that they be considered broadly as covering rosin materials containing those radicals as major constituents. Thus, the products derived from hydrogenated rosin are considered to have hydroabietyl radicals as the major constituent, and dehydrogenated rosin is considered to have dehydroabietyl radicals as the major constituent. Hydroabietylamine is thus considered synonymous with hydrogenated rosin amine, and dehydroabietylamine is considered synonymous with dehydrogenated rosin amine. It is not intended, however, to exclude the possibility of minor amounts of each of the various modified rosin amines in any of the rosin amines referred to by specific chemical names.

What I claim and desire to protect by Letters Patent is:

1. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% of nitric acid, about 1 to 5% of hydrofluoric acid and about 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula

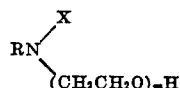


where R is a radical of the group consisting of dehydroabietyl and hydroabietyl, X is a radical of the group consisting of hydrogen and



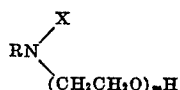
and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being within the range of 11 to 40.

2. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



where R is the dehydroabietyl radical, X is a radical of the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being within the range of 11 to 40.

3. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula

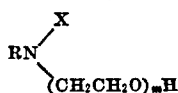


where R is the dehydroabietyl radical, X is a radical of the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, and m is an integer from 10 to 40 and n is an integer from 1 to 30 and the sum of m and n is about 28.

4. An aqueous pickling bath solution for stain-

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less steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula

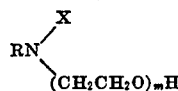


where R is the hydroabietyl radical, X is a radical of the group consisting of hydrogen and



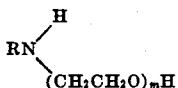
and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being within the range of 11 to 40.

5. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



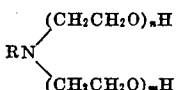
where R is the hydroabietyl radical, X is a radical of the group consisting of hydrogen and $-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, and m is an integer from 10 to 40 and n is an integer from 1 to 30 and the sum of m and n is about 28.

6. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% of nitric acid, about 1 to 5% of hydrofluoric acid, and about 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



where R is a radical of the group consisting of dehydroabietyl and hydroabietyl and m is an integer from 10 to 40.

7. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula

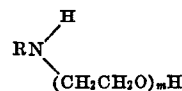


where R is a radical of the group consisting of dehydroabietyl and hydroabietyl, and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being within the range of 11 to 40.

8. An aqueous pickling bath solution for stainless steel containing, in amounts based on the

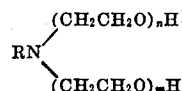
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weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



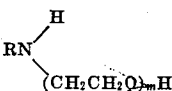
10 where R is the dehydroabietyl radical and m is an integer from 10 to 40.

9. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



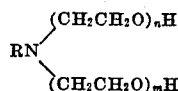
where R is the dehydroabietyl radical, and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being 28.

10. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



where R is the hydroabietyl radical and m is an integer from 10 to 40.

11. An aqueous pickling bath solution for stainless steel containing, in amounts based on the weight of the solution, besides a complement of water about 5 to 20% nitric acid, about 1 to 5% hydrofluoric acid, and 0.001 to 3% of a glycol ether of an ethanol rosin amine having the general formula



where R is the hydroabietyl radical, and m is an integer from 10 to 40 and n is an integer from 1 to 30, the sum of m and n being 28.

EDWARD A. BRIED.

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