

UNITED STATES PATENT OFFICE

2,355,599

ACID METAL TREATING BATHS

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No Drawing. Application January 23, 1941,
Serial No. 375,657

3 Claims. (Cl. 252-146)

This invention relates to the treatment of metals with acid solutions and particularly to the pickling or cleaning of metals such as iron or steel.

The pickling or cleaning of ferrous metal articles, e. g., articles of iron or steel, is commonly carried out by means of acid pickling baths which remove scale or oxide from the metal surface of the article. Acid baths are commonly used for that purpose although baths consisting of solutions of acid salts are also used. Such acid baths attack the scale or rust on the metal articles so as to remove the same and in addition to that action they also tend to attack or corrode the underlying metal. Such corrosive attack results in an excessive consumption of acid and also in a rough or pitted surface on the metal.

In order to overcome to a large extent the undesirable corrosive action of pickling baths upon the metal, it has been common practice to employ in such baths suitable small amounts of so-called "corrosion inhibitors". Formaldehyde is a substance which has been used to inhibit corrosion of such baths. However, ordinary formaldehyde is not as effective as desired.

It is an object of the present invention to provide an improved method of pickling or cleaning metal articles, particularly ferrous metal articles such as iron or steel articles. A further object is the provision of improved pickling or cleaning baths for this purpose, in which baths there is present an improved corrosion inhibitor. These and still further objects will be apparent from the ensuing description of the invention.

I have discovered that trioxane is an effective corrosion inhibitor for use in acid baths for the treatment of metals and particularly in metal cleaning and pickling baths, trioxane being markedly superior to ordinary formaldehyde for that purpose. Its action is to inhibit corrosion of the metal while permitting the acid to attack and remove from the metal rust and scale. Furthermore, the present use of trioxane does not interfere with subsequent electroplating of metal work as does the use of complex organic nitrogen compounds which leave on metal absorbed material which has an objectionable effect in subsequent plating operations. Accordingly, the above objects may be accomplished by subjecting metal articles to the action of an acid bath to which has been added a suitable amount of trioxane.

Acid baths containing trioxane are particularly useful for pickling and cleaning ferrous metal articles, but may also be used for the treat-

ment of nickel metal articles, and zinc and aluminum die castings and the like.

Trioxane, a cyclic trimer of formaldehyde which is known also as alpha-trioxymethylene, is a solid which melts at 63-64° C. and boils at 114° C. The compound is stable at normal temperatures, has a pleasing odor resembling chloroform. When pure, it has no odor of formaldehyde. It is soluble in water to the extent of about 20% by weight at 20° C. and is not decomposed in ordinary water solutions. The compound is also readily soluble in aqueous solutions of acids such as are used for metal pickling and cleaning purposes.

The superiority of trioxane for the present purpose over ordinary aqueous formaldehyde solutions such as formalin, has been shown by experiments employing various acid solutions as pickling baths. Thus, in one experiment an aqueous solution of hydrochloric acid containing 23 grams of hydrogen chloride and 1.64 grams of trioxane per 100 cc. of solution was found to be 16% less corrosive to iron strips placed in the bath than was a similar solution containing 5.5 grams of ordinary 37% formaldehyde solution in place of trioxane. The tests were carried out at ordinary temperatures during a period of 72 hours using 16 gauge iron strips in each case under substantially the same conditions. Furthermore, the solution containing trioxane lost 23% less formaldehyde, calculating the trioxane as formaldehyde, than did the solution containing ordinary aqueous formaldehyde.

The effectiveness of trioxane in sulfuric acid pickling baths was demonstrated by experiments employing in one case a sulfuric acid solution containing 30.6 grams H_2SO_4 and 0.35 grams of trioxane, and in the other case a similar solution containing 1 gram of 37% formaldehyde solution in place of trioxane per 100 cc. In both experiments 16 gauge black iron test strips of the same size and shape were immersed in the solution at a temperature of 80° C. The solution containing trioxane was found to have dissolved approximately 20% less iron over a period of 4 hours than had the corresponding solution containing ordinary formaldehyde.

From the above it is evident that trioxane is an effective corrosion inhibitor for acid pickling baths, being substantially more effective than ordinary formaldehyde. Such baths containing trioxane may be used in the same manner and for the same purposes as are the commonly employed acid pickling baths. The acid baths will generally contain in the neighborhood of 5-35%

by weight of acid depending upon the particular acid employed and may be used at ordinary temperatures or at elevated temperatures, e. g., temperatures in the neighborhood of 90° C. or higher. Acid baths containing larger or smaller concentrations of acid may be employed, although in general acid concentrations of at least 10% give better results than lower concentrations. The acid employed should be non-oxidizing since otherwise the trioxane would not long remain in the bath. By the term "non-oxidizing" I do not mean to exclude acids such as sulfuric acid which under some circumstances of use may be considered as oxidizing. However, acids such as nitric acid are definitely excluded by the term. Examples of acids which may be employed are hydrohalogen acids such as hydrochloric and hydrofluoric acids, sulfuric acid, phosphoric acid and the like mineral acids, including acid sulfates. The acids may contain substantial amounts of metal salts such as iron chloride, iron sulfate and the like. While in general it will be desirable to employ mineral acids of the type indicated, organic acid solutions, e. g., solutions of acetic acid, may under some circumstances be used, under which conditions trioxane may be added as a corrosion inhibitor.

The amount of trioxane employed may vary considerably. Amounts as low as 0.1% by weight are effective although amounts ranging from 0.2 to 2% are preferred. Higher concentrations may also be used although use of amounts in excess of 2% of the weight of the bath in general offers no additional advantage and is not recommended.

In employing pickling baths containing trioxane as inhibitor, the metal to be cleaned or pickled should, of course, be immersed in or contacted with the bath a sufficient length of time to effect the desired treatment after which the article will be washed to free it of acid. Instead of immersing the articles in the bath, they may be sprayed with the acid, or contacted therewith by various other means commonly known in the art. In the case of articles such as iron sheets, wire, rods and the like they may be passed through or dipped into the bath in a continu-

ous manner, the rate of passage through the bath being regulated so as to provide the proper time of contact.

The use of trioxane is superior to the use of formaldehyde for several reasons. Pickling baths containing trioxane smell little of formaldehyde. As is commonly known, the elimination or inhibiting of the odor of formaldehyde over pickling baths is a distinct advantage. Another advantage is that trioxane is a more effective corrosion inhibitor since by its use, there is generally from 12-16% less metal dissolved by the acid baths under substantially the same conditions of use than when formaldehyde is used as inhibitor. A still further advantage is the fact that trioxane is effective as a corrosion inhibitor in such baths over longer periods of time. This advantage is important since it permits the use of less inhibiting agent initially or at least it makes possible the operation of pickling baths for longer periods of time without requiring replenishment of the inhibitor.

As widely different modifications of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited by the details of the foregoing description and examples which, are intended to be illustrative only, except as indicated in the appended claims.

I claim:

1. The method of removing oxidic foreign matter from the surface of a metal which comprises subjecting a metal article to the action of a non-oxidizing acid bath containing 0.1 to 2% by weight of alpha-trioxymethylene as corrosion inhibitor.

2. The method of removing oxidic foreign matter from the surface of a metal which comprises subjecting a ferrous metal article to the action of a non-oxidizing acid bath containing 0.1 to 2% by weight of alpha-trioxymethylene as corrosion inhibitor.

3. An acid pickling and cleaning bath comprising a non-oxidizing mineral acid and 0.1 to 2% by weight of alpha-trioxymethylene as corrosion inhibitor.

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