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IRA H. DERBY, OF INDIANAPOLIS, INDIANA, ASSIGNOR TO PETER C. REILLY, OF INDIANAPOLIS, INDIANA

PROCESS OF PICKLING IRON AND STEEL

No Drawing.

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My invention relates to the pickling of metal articles, particularly iron or steel articles, or their alloys. More specifically, my invention relates to a process of reducing or inhibiting the solution of the metal article during the pickling operation.

In the manufacture of articles from iron, steel and their alloys, it is usual to subject the original ingot to a hot rolling step. For example, in the fabrication of steel plates, the original ingot is hot rolled to reduce the same to the desired size. During the process of working the ingot, it becomes covered with a thin superficial layer of blue black, mainly ferro-ferric oxide. For satisfactory results in subsequent processing, as for example, cold rolling, it is necessary to completely remove the oxide or scale as it is technically known, to develop a clean metallic surface. The cleaning may be accomplished mechanically by buffing or polishing but this is laborious and expensive since the oxide is a harder material than the steel and is spread over a large surface. In view thereof, a chemical process is usually employed for removing the oxide scale. The process usually consists in dipping the article to be cleaned in an acid bath as, for example, sulphuric acid, acid sulfates, preferably hot, or in cold dilute hydrochloric acid. The metal is allowed to remain in the cleaning bath for a short period of time, varying usually from ten to twenty minutes, after which it is withdrawn. Thereafter, the metal is washed with fresh water to remove that portion of the pickling solution adhering thereto. While this treatment effects a loosening of the oxide scale in the form of small black to reddish brown flocculent masses which fall away into the bath, it also allows a considerable amount of the metal to go into solution with an accompanying liberation of hydrogen gas.

It may also be pointed out that in some cases, the excessive solution of the metal results in the production of a pitted surface instead of a satiny, smooth, uniform surface which is desired in the finished commercial article.

It is the object of my invention to reduce

the solution of the metal in the pickling bath to a minimum in order to avoid the loss of valuable material, and objectionable pitting.

I have discovered that phosphorous-sulfur compositions which may comprise compounds or mixtures when added preferably in minute amounts, act to materially reduce or substantially prevent the solution in the pickling bath of iron or steel, or iron or steel alloys, and that at the same time the removal of the scale is satisfactorily accomplished. Substances which function as described are known as inhibitors since they protect the iron or steel material being pickled from attack by the pickling solution.

I have found that both soluble inorganic and organic phosphorous-sulfur compounds function satisfactorily as inhibitors in the pickling of iron and steel articles. As an example of inorganic compounds the reaction products of nitrogen compounds with penta sulfide of phosphorous have given excellent results. For example, the reaction product of ammonium hydroxide and penta sulfide of phosphorous have been found satisfactory. Various organic phosphorous-sulfur compounds may be used containing phosphorous and sulfur in combination with an aliphatic or aromatic radical. In the preferred form of my invention, I use organic nuclear phosphorous-sulfur compounds but, obviously, I do not desire to be limited to nuclear organic compounds. As an example of an aliphatic organic inhibitor containing phosphorous and sulfur, satisfactory results have been obtained with the reaction product of phosphorous pentasulfide and an alcohol such as ethyl alcohol. The homologues of the latter may be used to react with the pentasulfide as, for example, butyl alcohol. Aromatic compounds, including hydrocarbons and substituted hydrocarbons, such as phenols, cresols, xyenols, naphthols, their homologues, or mixtures of these compounds may be reacted with phosphorous pentasulfide to produce very satisfactory inhibitors. Excellent inhibitors may be produced by reacting phosphorous pentasulfide with organic acids, aldehydes and ketones. Pentasulfide of phosphorous may also be treated with nitrogen

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derivatives such as the amines, nitriles and pyridine bases and the reaction products thereof used as inhibitors.

The following examples are illustrative of my invention:

1. Denatured alcohol was reacted with 20%, by weight, of phosphorous pentasulfide for an hour at its boiling point and the liquid reaction product was employed with the following results: An amount equal to .1% of the pickling bath which consisted of 5% sulphuric acid was added. The temperature of the bath was raised to 80° C. and a test piece of steel plate was immersed in the bath for fifteen minutes. The entire loss was found to be .6% which represented the scale. The test piece was replaced in the bath, maintained at the same temperature, for a subsequent period of thirty minutes. A metal loss of less than .04% resulted. It is believed that the major reaction product formed by the reaction of alcohol with phosphorous pentasulfide is tri ethanol tetra thio phosphoric acid. However, I do not desire to be limited to any specific reaction product but content myself with calling the reaction product that obtained by the reaction of alcohol with phosphorous pentasulfide.

2. Cresylic acid was reacted with 20%, by weight, of phosphorous pentasulfide for an hour at 120° C. The liquid reaction product was employed with the following results: An amount equal to .1% of the pickling bath which consisted of 5% sulphuric acid was added. The temperature of the bath was raised to 80° C. and a test piece of steel plate was immersed in the bath for fifteen minutes. The entire loss was found to be .6% which represented the scale. The test piece was replaced in the bath, maintained at the same temperature, for a subsequent period of thirty minutes. A metal loss of less than .02% resulted. It is believed that the major reaction product formed by the reaction of cresylic acid with phosphorous pentasulfide is tri cresol tetra thio phosphoric acid. However, I do not desire to be limited to any specific finished reaction product but content myself with calling the reaction product that obtained by the reaction of cresylic acid and phosphorous pentasulfide.

3. Benzaldehyde was reacted with phosphorous pentasulfide, giving an oily product, which was used in the quantity of .1% of the pickling bath, yielding a metal loss of the order of .01%. This example is broadly representative of the preparation and use of the reaction product of an aldehyde and a phosphorous sulphur compound.

4. As representative of the ketone class of compounds, the following is given. At the boiling point of acetone, the reaction with phosphorous pentasulfide is relatively slow, thereby producing a very dilute mixture of the active sulphur compound. This dilute

mixture may be utilized as an addition to the pickling bath. Satisfactory results were obtained when the acetone product was added to the bath in the amount of .1% of the pickling bath, the metal loss being of the order of .15%.

5. The following is an example of the use of amine reaction products. Aniline reacts rapidly with phosphorous pentasulfide and forms a solid product which is insoluble in water. This product, however, is soluble in cresylic acid. A one to one mixture of the insoluble product was made with the solvent and .1% of this solution, based on the weight of the pickling bath, was added to the bath, resulting in a metal loss of .07%.

6. Benzonitrile was reacted with phosphorous pentasulfide, yielding a product which when added to the pickling bath in the amount of .1%, based on the weight of the pickling bath, gave a metal loss of the order of .05%.

7. As is illustrative of the use of a pyridine base, the following example is given. A fraction of pyridine oil boiling between 240° and 280° C. was obtained and reacted with 10% of phosphorous pentasulfide, giving a clear oil as a product. .1% of this oil, based on the weight of the bath when added to the bath, gave a metal loss of .02%. It appeared to have the same effective inhibiting property as the product formed by reacting cresylic acid with phosphorous pentasulfide.

8. Various hydrocarbons may be reacted with phosphorous pentasulfide to form effective inhibitors. For example, naphthalene was heated to 200° C. with phosphorous pentasulfide, producing a resinous product insoluble in water and therefore not in itself an inhibitor. The compound of naphthalene and phosphorous pentasulfide is soluble in cresylic acid. When dissolved in this medium and added in quantities of .1% to the pickling bath, a metal loss of the order of .02% was observed. Naphthalene has been given as an illustration of the use of an aromatic hydrocarbon. However, the following hydrocarbons may also be reacted with pentasulfide to produce a suitable inhibitor: coal tar distillates, including the lighter distillates, the heavier distillates, or the intermediate distillates, or a mixture of any or of all of these distillates, water gas distillates, oil tar distillates, wood tar distillates and similar oils or mixtures thereof. Referring to the coal tar distillates, they may be used in the crude or refined state or after the addition thereto or the removal therefrom of various coal tar constituents. Instead of using naphthalene anthracene may be used to react with phosphorous pentasulfide to form an inhibitor. The compounds referred to above are merely illustrative of suitable hydrocarbons and are not to be

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taken as limiting the kind of hydrocarbon which may be used.

9. Phosphorous pentasulfide reacts with ammonia, producing a class of compounds which may be given the general name of thio phosphoric acid amines. These inorganic compounds form suitable inhibitors. For example, phosphorous pentasulfide was reacted with ammonium hydroxide solution, giving a product which was added in the quantity of .1% of the pickling bath. A metal loss of .13% was shown.

While I have set forth a number of methods for the preparation of the phosphorous-sulfur inhibitors, they are obviously merely illustrative and not by any way of limitation. I desire to point out that my invention resides broadly in the addition of a soluble phosphorous-sulfur composition to the pickling bath to inhibit the solution of the article being pickled regardless of the methods used for the preparation of the inhibiting agent. While I have given examples showing reacting a phosphorous-sulfur compound with an organic compound, it is obvious that the inhibitor may be prepared by reacting a compound containing phosphorous with one containing sulfur. For example, an organic compound may have sulfur introduced therein and the sulphidized compound reacted with a phosphorous compound, or the organic compound may have phosphorous introduced therein and reacted with a sulphur containing compound. Other analogous methods of preparation will readily suggest themselves to those skilled in the art.

It is to be understood that my invention is not limited to the pickling of iron and steel per se but includes iron and steel alloys such as chromium alloys, nickel alloys, titanium alloys, and tungsten alloys.

While I have stated that in the usual case the percentage of inhibitor added to the pickling bath is .1%, based on the weight of the bath, it is to be understood that this percentage may be considerably varied, either above or below, depending on the character of the steel or alloy of steel being treated, and the efficiency of the inhibitor.

My invention may be practiced in connection with any of the pickling mediums or baths usually used. While it is preferred to use sulphuric acid, examples of other suitable baths are acid sulfates and hydrochloric acid.

I claim:

1. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto a soluble inhibitor containing phosphorous and sulfur.

2. The process of substantially preventing the solution of iron and steel articles in a pickling bath having sulfuric acid as its essential constituent comprising adding to

the bath a soluble inhibitor containing phosphorous and sulfur.

3. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto a relatively small proportion of a soluble inhibitor containing phosphorous and sulfur.

4. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto a soluble organic inhibitor containing phosphorous and sulfur.

5. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto a soluble nuclear organic inhibitor containing phosphorous and sulfur.

6. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto a soluble aromatic organic inhibitor containing phosphorous and sulfur.

7. The process of substantially preventing the solution of iron and steel articles in a pickling bath comprising adding thereto an inhibitor consisting of the reaction product of phosphorous pentasulfide and a hydroxy holding compound.

8. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising a pickling medium and a soluble inhibitor containing phosphorous and sulfur.

9. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising sulfuric acid and a soluble inhibitor containing phosphorous and sulfur.

10. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof comprising a pickling medium and a relatively small proportion of a soluble inhibitor containing phosphorous and sulfur.

11. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising a pickling medium and a soluble organic inhibitor containing phosphorous and sulfur.

12. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising a pickling medium and a soluble nuclear organic inhibitor containing phosphorous and sulfur.

13. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising a pickling medium and a soluble aromatic organic inhibitor containing phosphorous and sulfur.

14. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof,

comprising a pickling medium and the reaction product consisting of phosphorous pentasulfide and a hydroxy holding compound.

- 5 15. A pickling bath adapted to effect the usual cleaning of iron and steel articles present therein and inhibit solution thereof, comprising a pickling medium and a soluble inhibitor containing phosphorous and sulfur
10 in amount approximately equal to .1% of the weight of the bath.

In testimony whereof I have signed my name to this specification.

IRA H. DERBY.

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