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## UNITED STATES PATENT OFFICE

JAMES H. GRAVELL AND ALFRED DOUTY, OF ELKINS PARK, PENNSYLVANIA; SAID GRAVELL ASSIGNOR TO AMERICAN CHEMICAL PAINT COMPANY, OF AMBLER, PENN-SYLVANIA, A CORPORATION OF DELAWARE

MATERIAL FOR SELECTIVELY CONTROLLING METAL-PICKLING BATHS

No Drawing.

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This invention relates broadly to the art of pickling and specifically to selectively controlling the action of pickling baths.

The objects of the invention are to save said, to save metal, to minimize the escape of abnoxious fumes, to avoid discoloration of the work, to prevent overpickling, to prolong the life of pickling baths, to save time, to conserve health, and to generally improve 10 the art of pickling.

We have practiced pickling according to the method described in U. S. Patent No. 288,150 and we have noted that the results are beneficial, but there are numerous disad-15 vantages which limit the utility of that method. We have found that the addition of potassium cyanide to the pickling baths not only prevents acid brittleness, but also tends to cause the action to be selective, in that 20 after the scale is removed the metal is protected to a great extent against the action of the acid. But to offset these advantages, the work is discolored, poisonous gas escapes from the bath and the desirable action of 25 the potassium cyanide is not lasting.

It occured to us that an improvement might be effected by adding the potassium cyanide in small increments and although this prolonged the life of the cyanide it did not over-30 come the discoloration of the work or the escape of poisonous fumes.

We have discovered that if we replaced the potassium cyanide by a substance that would react with the nascent hydrogen, developed by the reaction between the acid bath and the metal being pickled, to liberate hydrocyanic acid within the bath, new and surprising results were obtained, the bath ceased to stain the work or to liberate a noticeable or objectionable amount of poisonous fumes, and a very small quantity of the added substance produced a powerful and lasting effect in selectively controlling the bath, in that after the oxide or scale was removed from the work, the corrosive effect of the bath on the work was materially reduced or checked.

Based on our discovery, we have invented a commercial process and a pickling adjunct which we will now describe.

We have found, as a class, that the thiocyanates react well with nascent hydrogen to furnish hydrocyanic acid within the pickling bath. Among these we prefer to use ammonium thiocyanate due to its commercial 55 availability.

In one way of practicing our invention, we prepare a pickling bath for cleaning steel consisting of:

1000.00 gallons 60 Sulphuric acid (66° Baumé) 50.00 gallons Ammonium thiocyanate\_\_\_\_ .50 pounds

This bath we maintain at a temperature of 180° F. more or less. When the steel to be 65 cleaned is introduced into this bath, the scale is quickly removed, after which the action of the bath is automatically checked or reduced to such an extent that even if the cleaned work is allowed to remain in the 70 bath for a long period it shows no ill effects.

Although the corrosive action of the acid on the metal is materially reduced, it is not stopped altogether and consequently hydrogen still escapes from the bath. The hydro-75 gen rises to the surface of the bath forming unstable bubbles which break and throw a spray of acid bath into the air to the great detriment of health and materials in the vicinity. In order to overcome this disad- 80 vantage we may add, in addition to thio-cyanate, a foaming agent.

We have investigated the compatibility of the various foaming agents and thiocyanate and find that they are not only compatible 85 but that the selective controlling effect is improved by the simultaneous use of these dissimilar classes of materials. Although rye meal liquor, saponin, and the like may be used to advantage, we prefer to use cellulose pulp waste liquor. This we may add to the bath as follows:-

Sulphuric acid (66°) \_\_\_\_\_ 50.00 gallons Ammonium thiocyanate 50.00 gallons 95 1.00 pound Ammonium thiocyanate\_\_\_\_ Cellulose pulp waste liquor\_\_ .50 gallons

The foaming agent makes the bubbles produced on the surface of the bath stable, with the result that the bath covers itself with a 100 Color of the fine of

blanket of foam, which holds the escaping hydrogen long enough for it to deposit its moisture before mingling with the air and thus prevents objectionable acid spray.

For convenience we may compound thiocyanate and the foaming agent in advance, to form an admixture, thus simplifying the individual proportioning of the several ingredients. To do this we admix the two in the following proportions:—

Cellulose pulp waste liquor\_\_\_\_\_ .50 gallons Ammonium thiocyanate\_\_\_\_\_ 1.00 pound

This forms about one half gallon of our 15 admixture which is sufficient for treating a

bath of the size given above.

If the admixture is to be transported, it is more convenient, if it is prepared in the dry state. In that case we select a dry foaming agent, like saponin or evaporated cellulose pulp liquor, and proportion them as follows:—

Evaporated cellulose pulp waste

liquor \_\_\_\_\_\_ 2.00 pounds Ammonium thiocyanate \_\_\_\_\_ 1.00 pound

It should be noted that although we have specified certain quantities of the ingredients in relation to the size of the pickling solution, the proportions of water, acid, control material and foaming agent may be varied through a great range without deviating from the spirit of this invention, as the effect produced by each ingredient may be increased or diminished by varying its concentration, as individual tastes will dictate.

We have found that not only sulphuric acid
may be used in our invention but that hydrochloric or phosphoric acid may also be used,
to but as sulphuric acid is in more general use
for the purpose of pickling, we have described our invention in connection with that

acid.

We claim:
1. A pickling bath for metal comprising an admixture of water, acid and a thiocyanate.

2. A pickling bath for metal comprising an admixture of water, acid, and ammonium thiocyanate.

JAMES H. GRAVELL. ALFRED DOUTY.