United States Patent Office 2,823,184 Patented Feb. 11, 1958

2,823,184

COMPOSITION AND PROCESS FOR METAL PICKLING

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No Drawing. Original application February 11, 1950, Serial No. 143,822, now Patent No. 2,664,408, dated December 29, 1953. Divided and this application March 23, 1953, Serial No. 349,952

15 Claims. (Cl. 252—149)

This invention relates to metal pickling and to new compositions particularly useful in this field.

The present application is a division of applicants' copending application Serial No. 143,822, filed February 11, 1950, which has now matured into Patent No. 2,664,408, issued on December 29, 1953.

In the pickling of metals, i. e. removal of scale or other metal oxidation products from metal surfaces, it is customary to treat the metal with a dilute aqueous solution of a relatively strong acid such as sulfuric or hydrochloric acid. In prior art practices, a compound or compounds which exhibit inhibiting properties are usually incorporated in such pickling acid in an effort to lessen the attack on the metal. For example, various coal tar products, sulfonated petroleum or alcoholic still residues, aromatic thiourea derivatives, and reaction products of certain aryl thioureas and an aldehyde have been stated to have inhibiting properties. It has also been suggested heretofore that the addition of such materials as cellulose pulp waste liquor and gelatin may increase the efficiencies of some pickling baths.

We have now discovered that the solid condensation products obtained by reacting urea, thiourea, or a mixture of urea and thiourea with a mixture of acidified sulfite pulp waste liquor and a water-soluble aldehyde in the presence of an acid catalyst exhibit markedly improved inhibiting properties against metal attack by acid pickling baths containing non-oxidizing acids as compared to prior art products.

Though we do not wish to be limited by any theoretical explanation, it is believed that the surprisingly superior inhibiting properties of the products obtained may be attributed in part to a reaction in addition to the expected condensation of urea or thiourea with aldehyde, namely a chemical reaction between at least some of the constituents of the sulfite pulp waste liquor and one or more of the other constituents. The composition of sulfite pulp waste liquor varies somewhat with the source and treatment, but usually consists of some inorganic materials such as calcium sulfate, calcium oxide and water, thio acids, other acids, chiefly lignosulfonic acid and their calcium salts, lignin, dextrose, mannose, gums, albumins, resins, vanillin and fermentable sugars. Of these the more important constituents are believed to be lignosulfonic acid, lignin, dextrose, mannose and vanillin. Whatever the explanation, we have found that the product of the above described reaction is markedly superior in metal pickling inhibiting properties to a mixture of the components, considered individually or in any combination thereof, e. g. a mixture of urea- or thiourea-aldehyde condensation product and sulfite pulp waste liquor. Thus, in a typical instance, we found that a urea-formaldehyde-sulfite waste liquor product made according to our invention gave almost 50% increased metal protection as compared to equivalent quantities of a mixture of sulfite pulp waste liquor and a urea-formaldehyde condensation product. Excellent results are achieved on metals such as various types of steels, iron, stainless steel, tinned steel, tinned copper, and tin.

In general, we incorporate our new condensation product in a pickling bath of the type customarily employed for cleaning metal objects, usually an aqueous solution containing from 1 to 50% by weight of a relatively strong non-oxidizing inorganic acid such as sulfuric, phosphoric, hydrochloric or hydrofluoric acid, preferably in 5–20% by weight of sulfuric acid or 5–30% hydrochloric acid. In some instances beneficial results may be achieved by incorporating our condensation product in aqueous mixtures of these and other acids. Furthermore, we have found that our new product may advantageously be admixed with other materials known to aid or exhibit inhibiting properties; for example, glue, sodium chloride and diphenylthiourea may be admixed therewith.

As illustrative of a method of preparing our condensation product, we mix urea, thiourea, or both, with sulfite pulp waste liquor and a water-soluble aldehyde in an acid reaction medium. Thus, urea and/or thiourea may be dissolved in water and the other two reactants added thereto. The resulting mixture may then be acidified and the precipitate which forms separated and dried. In preparing the condensation products of our present invention the sulfite pulp waste liquor used should preferably not contain more than 30 grams lignone (i. e. 15 grams of the total solids of the waste liquor) per 15 grams urea, thiourea or mixtures of urea and thiourea employed. If higher concentrations are used, the acid inhibiting properties of the resulting product are found to be unsatisfactory. We have obtained the best results by using, in the condensation reaction, sulfite pulp waste liquor concentrations of about 2.5 grams lignone (1.25 grams solid waste liquor) per 15 grams of urea and/or thiourea. However, considerably lower concentrations of the sulfite pulp waste liquor can be employed, excellent acid inhibiting materials being obtained when concentrations as low as 0.5 grams lignone to 15 grams of urea and/or thiourea are used.

The effect of varying the amount of lignone in the condensation reaction is best illustrated by the table given in Example 1. The products obtained in each instance were washed with water, then with alcohol and air dried. Each product was tested by using 0.025% by weight of the product in a pickling bath of 10% sulfuric acid in which was immersed a steel strip, the bath being maintained at a temperature of 80° C. during the test.

EXAMPLE 1

Variation of sulfite pulp waste liquor (lignone) concentration HCl *catalyst*

Urea, Grams	Thiourea, Grams	Formalin, Grams	Lignone, Grams	Weight Yield, Percent	Percent Protection
13.5	1.5	20.25	2.5	74.4	87.6
13.5	1.5	20.25	5.0	74.8	86.7
13.5	1.5	20.25	10.0	74.2	86.9
13.5	1.5	20.25	15.0	74.0	87.0
13.5	1.5	20.25	20.0	69.2	86.6
13.5	1.5	20.25	30.0	69.1	81.4

The product, prepared according to our invention, is incorporated in a typical acid pickling bath, either alone or in conjunction with other materials which are known to exhibit inhibiting properties. A comparatively low concentration of our inhibitor is sufficient to obtain good metal protection. The concentration required to achieve a certain amount of metal protection will vary with the pickling conditions, but the quantity required is significantly lower than that of heretofore known inhibiting materials. Thus, we have found that a concentration, in acid baths of 5 to

10% acid, of as little as 0.001% by weight is effective under usual pickling conditions while about 0.025% by weight is the usual preferred concentration, and 0.10% is the usual maximum amount necessary, though more may be used, 7% being about the maximum amount which will dissolve in the acid pickling bath.

To illustrate our method of preparation by a specific example, we may dissolve 60 parts of urea and 6 parts of thiourea in 89 parts of water. 89 parts of sulfite pulp waste liquor (containing about 12% solids) and 89 parts of 37% formaldehyde are added and the solution stirred. Alternatively, a concentrated sulfite pulp waste liquor may be used with a corresponding addition of water. 1.5 parts of hydrochloric acid are added with stirring. A precipitate soon forms which may be separated and washed with water, followed by oven drying at 100° C. The product so obtained is superior in inhibiting properties to those of the prior art, and may be admixed with other materials of inhibiting value, such as diphenylthiourea, glue, etc. To obtain a preferred product we admix:

45% of our condensation product prepared as described above
19% glue
19% sodium chloride
15% diphenylthiourea
2% of a wetting agent such as the commercially available wetting agents of the aryl alkyl polyether alcohol type

Our invention is not limited to any specific reaction product resulting from the condensation reaction of a water-soluble aldehyde, sulfite pulp waste liquor, urea and/or thiourea since we have found that the condensation reaction product will have superior acid inhibiting properties as long as a water-soluble aldehyde having less than two functional groups other than the aldehyde group is used, the aldehyde to urea and/or thiourea ratio of the reaction mixture is maintained to within 0.1 to 5 mols aldehyde per mol of urea and/or thiourea, and the concentration of the sulfite pulp waste liquor does not exceed 30 grams lignone, or 15 grams solid waste liquor, per 15 grams of urea and/or thiourea employed. The table of Example 2, which gives some of the reaction ratios employed, helps further to illustrate the wide range of urea and/or thiourea reactants to aldehyde reactants that can be employed while practicing our invention. In studying this table, it should be kept in mind that the lignone can be varied, as illustrated in Example 1, for each ratio of urea and/or thiourea to aldehyde given in Example 2. However, for ease of illustration, the amount of urea and thiourea reactants of Example 1 has been kept constant whereas the amount of lignone present in the reactants of Example 2 has been kept constant. The resulting product of each of the reaction ratios given in Example 2 was found on testing to be an excellent acid inhibitor. The tests were carried out in the same manner as described for Example 1.

EXAMPLE 2

Urea and thiourea-aldehyde reactions in the presence of sulfite pulp waste liquor HCl *catalyst*

Urea and Thiourea, Mols	Aldehyde, Mols	Lignone, Grams
1 Urea	0.5 Formaldehyde	7.5
Do	0.1 Formaldehyde	7.5
Do	1 Benzaldehyde	7.5
Do	5 Butyraldehyde	7.5
Do	0.33 Butyraldehyde	7.5
1 Thiourea	1 Formaldehyde	10.0
Do	5 Formaldehyde	10.0
Do	0.125 Formaldehyde	10.0

In the following examples, which illustrate but do not limit our invention, the composition of the specific example set forth on page 5 was used, and is designated therein simply as the "inhibitor." The loss in weight of the metal after pickling with and without the presence of the inhibitor gives the "percent protection" according to the expression:

$$\frac{(\text{Weight loss uninhibited}) - (\text{Weight loss inhibited})}{(\text{Weight loss uninhibited})} \times 100$$

EXAMPLE 3

These data were obtained by pickling at various temperatures strips of cold rolled steel in baths of 6% hydrochloric acid containing the indicated quantities of inhibitor:

Inhibitor Concentration (Weight percent)	Percent Protection		
	25° C.	50° C.	80° C.
.005	81.3	76.2	81.0
.010	86.7	79.8	84.2
.025	94.6	81.5	87.4
.050	95.0	84.8	96.4
.100	96.1	90.0	97.4

EXAMPLE 4

These data were obtained by pickling at 80° C. strips of different steels in baths of 10% sulfuric acid containing the indicated quantities of inhibitor:

Sample	Percent Protection at the Indicated Inhibitor Concentration in Weight Percent			
	.005	.010	.020	.050
Steel 1	86.4	95.4	97.5	97.5
Steel 2	75.7	83.8	91.3	99.0
Steel 3	61.4	80.5	83.9	92.0
Steel 4	84.4	90.5	97.4	100.0

EXAMPLE 5

These data were obtained by pickling, at 25 or 50° C. strips of steel in 10% hydrofluoric acid baths containing various quantities of inhibitor:

Inhibitor Concentration (Weight percent)	Percent Protection	
	25° C.	50° C.
0.01	64.8	85.5
0.05	76.5	87.5
0.10	85.8	89.4

EXAMPLE 6

This example shows the excellent metal protection properties of our products when used in relatively high strength hydrofluoric acid pickling baths, and also demonstrates high stability and long lasting qualities. These data were obtained by pickling, at 24° C., steel strips in a bath of 60% hydrofluoric acid containing 0.50% by weight of our inhibitor for the period of time indicated:

Time (hours)	Percent Protection
23	99.9
72	99.9
288	99.9
408	99.9
768	99.9

Similar pickling operations were carried out employing inhibitor compositions made from urea in the absence of thiourea, from thiourea without urea present, and from mixtures of urea and thiourea other than the above-described mixtures, and marked improvement in metal protection was noted in each case. Similarly, aldehydes other than formaldehyde, e. g. acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde or aldol, may be employed in the condensation reaction, and considerable modification is possible in the choice of materials to be

admixed with our condensation products without departing from our invention.

Having thus described our invention, we claim:

1. In the process of pickling metal surfaces the improvement which comprises subjecting the surface to the action of an aqueous solution of a non-oxidizing pickling acid, said solution containing 0.001 to 7% by weight of a reaction product resulting from an acidified reaction mixture containing sulfite pulp waste liquor, water-soluble aldehyde and material selected from the group consisting of urea and thiourea, in which reaction mixture 0.1 to 5 mols of water-soluble aldehyde are present per mol of said material of said group and said sulfite pulp waste liquor contains not more than 1 gram of sulfite waste liquor solids per gram of material of said group.

2. The process of claim 1 wherein said surface is steel and said aldehyde is formaldehyde.

3. The process of claim 1 wherein said pickling acid has a concentration of 1 to 50%.

4. The process of claim 3 wherein said surface is steel and said pickling acid is sulfuric acid.

5. The process of claim 3 wherein said surface is steel and said pickling acid is hydrochloric acid.

6. The process of claim 3 wherein said surface is steel and said pickling acid is hydrofluoric acid.

7. The process of claim 3 wherein said surface is steel and said material of said group is urea.

8. The process of claim 3 wherein said surface is steel and said material of said group is thiourea.

9. A pickling bath comprising an aqueous solution of a non-oxidizing inorganic pickling acid, said solution containing 0.001 to 7% by weight of the condensation product resulting from an acidified reaction mixture of sulfite pulp waste liquor, water-soluble aldehyde, urea and thiourea in which reaction mixture 0.1 to 5 mols of aldehyde are present per mol of combined urea and thiourea and said sulfite pulp waste liquor contains not more than 1 gram of sulfite pulp waste liquor solids per gram of combined urea and thiourea.

10. A pickling bath comprising an aqueous solution of a non-oxidizing inorganic pickling acid, said solution containing 0.001 to 7% by weight of the condensation product resulting from an acidified reaction mixture of sulfite pulp waste liquor, water-soluble aldehyde, and urea in which reaction mixture 0.1 to 5 mols of aldehyde are present per mol of combined urea and said sulfite pulp waste liquor contains not more than 1 gram of sulfite pulp waste liquor solids per gram of urea.

11. A pickling bath comprising an aqueous solution of a non-oxidizing inorganic pickling acid, said solution containing 0.001 to 7% by weight of the condensation product resulting from an acidified reaction mixture of sulfite pulp waste liquor, water-soluble aldehyde, and thiourea in which reaction mixture 0.1 to 5 mols of aldehyde are present per mol of combined thiourea and said sulfite pulp waste liquor contains not more than 1 gram of sulfite pulp waste liquor solids per gram of thiourea.

12. A pickling bath comprising an aqueous solution of sulfuric acid containing 0.001 to 7% by weight of the condensation product obtained from an acidified reaction mixture containing sulfite pulp waste liquor, water-soluble aldehyde and materials selected from the group consisting of urea and thiourea, in which reaction mixture 0.1 to 5 mols of the water-soluble aldehyde are present per mol of said material of said group and said sulfite pulp waste liquor contains not more than 1 gram of sulfite waste liquor solids per gram of said material of said group.

13. A pickling bath comprising an aqueous solution of hydrochloric acid containing 0.001 to 7% by weight of the condensation product obtained from an acidified reaction mixture containing sulfite pulp waste liquor, water-soluble aldehyde and materials selected from the group consisting of urea and thiourea, in which reaction mixture 0.1 to 5 mols of the water-soluble aldehyde are present per mol of said material of said group and said sulfite pulp waste liquor contains not more than 1 gram of sulfite waste liquor solids per gram of said material of said group.

14. A pickling bath comprising an aqueous solution of hydrofluoric acid containing 0.001 to 7% by weight of the condensation product obtained from an acidified reaction mixture containing sulfite pulp waste liquor, water-soluble aldehyde and materials selected from the group consisting of urea and thiourea, in which reaction mixture 0.1 to 5 mols of the water-soluble aldehyde are present per mol of said material of said group and said sulfite pulp waste liquor contains not more than 1 gram of sulfite waste liquor solids per gram of said material of said group.

15. A pickling bath comprising an aqueous solution of phosphoric acid containing 0.001 to 7% by weight of the condensation product obtained from an acidified reaction mixture containing sulfite pulp waste liquor, water-soluble aldehyde and materials selected from the group consisting of urea and thiourea, in which reaction mixture 0.1 to 5 mols of the water-soluble aldehyde are present per mol of said material of said group and said sulfite pulp waste liquor contains not more than 1 gram of sulfite waste liquor solids per gram of said material of said group.

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