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INHIBITOR

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This invention relates to inhibitors, that is, to substances which protect steel and similar materials from corrosion by acids in the process of pickling metals.

It is common in the steel industry, particularly in the manufacture of steel sheets or other shapes which are to be coated with a protective coating, such as zinc or cadmium, to first clean the surface of the steel in order that the subsequent coating material may adhere firmly thereto, without danger of the coating peeling off. This treatment consists in providing a dilute solution of an acid, such as sulphuric acid, called a "pickling" bath, holding the solution at a predetermined temperature, usually above room temperature and immersing the steel pieces therein for a length of time sufficient to remove scale and other matter from the surface of the steel. The acid tends to attack the steel and there is added to the pickling solution a small amount of a substance, called an "inhibitor", to protect the steel from attack by the acid, while still allowing the acid to act on and remove such surface material from the steel as is detrimental in the subsequent coating operation.

The present invention is intended to provide an inhibitor which is easily prepared, which is low in cost and which is highly effective in a pickling solution in very small amounts.

I have discovered that substances which might be termed broadly aldehyde-aromatic amine compounds are effective for this purpose. Among such compounds are ethylidene-aniline which is formed, as is well known by the action of acetaldehyde on aniline, and toluidine-acetaldehyde, which is formed by the action of acetaldehyde on mixed toluidines.

The reaction of acetaldehyde on aniline to form ethylidene-aniline may be represented as follows:

$$CH_3.CHO+C_6H_5.NH_2 \rightarrow C_6H_5.N=\overset{H}{\underset{|}{C}}CH_3+H_2O$$

The generic formula for the aldehyde-aromatic amine compounds may be represented as follows:

$$R-N=\overset{H}{\underset{|}{C}}-R'$$

in which R represents an aryl group and R' represents an alkyl group.

Although I have found that substances of this character are highly efficient as inhibitors, the effectiveness thereof may be increased by certain treatments.

1. I have found that when ethylidene-aniline and other aldehyde-aromatic amine compounds are heated, say to 100° C. either with a reflux condenser or without any condenser for an appreciable period of time, say from ½ hour to 1½ hours, the material becomes viscous. The material so treated is more effective as an inhibitor than the original substance.

2. I have found that ethylidene-aniline and other aldehyde-aromatic amine compounds if heated with sulphur, for example, at about 100° C. with a reflux condenser for a substantial period of time, say about 1½ hours, the resulting product is far more effective than the original compound or even than the compound as treated in accordance with the procedure outlined in the above paragraph 1. The amount of sulphur may vary and I have used from 5 to 15 per cent of sulphur with excellent results. These sulphurized compounds are of indefinite structure in which the sulphur appears to be added on to the rest of the molecule, but in any event it appears that these compounds are not of the nature of thio-aldehydes since they do not

give off hydrogen sulphide as do such compounds.

The substances constituting the subject matter of my invention were tested in a pickling bath in the following manner:

A pickling solution consists of 250 cc. of 6 per cent by weight of 66° Bé. sulphuric acid. the solution being held at a temperature of 183° to 185° F. The steel pieces used were ¾" wide by 3½" long and were placed in the pickling solution and allowed to remain for varying lengths of time. Several runs were made without any inhibitor and other runs were made with a number of inhibitors in varying amounts in accordance with the present invention. The table given below shows the relative results obtained when no inhibitor was used and when the inhibitors of the ethylidene-aniline type described above were used:

Reagent	Amount of reagent grams	Weight of metal grams			W grams		Per cent loss	
		At start	20 min.	40 min.	20 min.	40 min.	20 min.	40 min.
A	0.075	3.973	3.955	3.938	0.018	0.035	0.45	0.88
	0.225	3.907	3.901	3.896	0.006	0.011	0.15	0.28
	0.375	3.901	3.895	3.891	0.006	0.010	0.15	0.36
B	0.075	4.052	4.023	4.005	0.029	0.047	0.72	1.16
	0.225	4.049	4.039	4.030	0.010	0.019	0.25	0.47
	0.375	3.935	3.930	3.920	0.005	0.015	0.21	0.38
C	0.075	4.045	4.000	3.960	0.045	0.085	0.12	2.10
	0.225	3.777	3.768	3.758	0.009	0.019	0.24	0.50
	0.375	3.870	3.867	3.852	0.008	0.018	0.21	0.47
D	0.075	3.844	3.824	3.808	0.020	0.036	0.52	0.94
	0.225	3.840	3.835	3.828	0.005	0.012	0.13	0.31
	0.375	3.685	3.676	0.670	0.009	0.015	0.24	0.41

Reagent	Amount of reagent grams	Weight of metal grams			△ W		Per cent loss		Average per cent loss in 40 min.
		At start	After 20 min.	After 40 min.	20 min.	40 min.	20 min.	40 min.	
None		3.723	1.590	Metal complete dissolved	2.133		57.0	100.0	
None		3.726	1.480		2.246		60.0	100.0	100.0
Ethylidene aniline (original)	0.025	3.976	3.182	2.020	0.794	1.956	20.0	49.0	
	0.025	3.906	3.154	2.030	0.752	1.876	19.2	48.0	48.5
	0.125	3.962	3.888	3.730	0.074	0.232	1.87	5.84	
	0.125	4.155	4.058	3.850	0.097	0.305	2.33	7.32	6.53
Ethylidene aniline (heated 1.5 hours under reflux)	0.025	4.130	3.453	2.181	0.677	1.949	16.40	74.2	59.4
	0.025	3.917	3.363	2.165	0.554	1.752	14.10	44.6	
	0.125	3.898	3.815	3.543	0.083	0.355	2.14	0.10	
	0.125	4.001	3.913	3.639	0.088	0.362	2.18	9.00	9.05
Ethylidene aniline (heated ½ hour in open dish)	0.025	3.977	3.552	2.234	0.425	0.743	10.5	18.7	
	0.025	3.945	3.310	1.841	0.635	1.104	16.1	28.9	23.8
	0.125	3.965	3.905	3.326	0.060	0.639	1.51	16.10	
	0.125	4.050	3.996	3.465	0.054	0.585	1.34	14.50	15.3
Ethylidene aniline plus 5% S	0.025	3.910	3.888	3.852	0.022	0.058	0.56	1.48	
	0.025	3.779	3.745	3.677	0.034	0.102	0.90	2.72	2.10
	0.125	4.020	4.015	4.008	0.005	0.012	0.12	0.30	
	0.125	4.055	4.048	4.041	0.007	0.014	0.17	0.35	.33
Ethylidene aniline plus 10% S	0.025	3.952	3.893	3.858	0.059	0.094	1.50	2.37	
	0.025	4.022	3.943	3.875	0.079	1.147	1.98	3.66	3.02
	0.125	3.795	3.783	3.773	0.012	0.022	0.32	0.58	
	0.125	3.623	3.613	3.602	0.010	0.021	0.28	0.58	0.58
Ethylidene aniline plus 15% S	0.025	4.030	4.002	3.965	0.028	0.065	0.70	1.61	
	0.025	3.795	3.770	3.745	0.025	0.050	0.66	1.33	1.47
	0.125	3.903	3.893	3.885	0.010	0.018	0.25	0.46	
	0.125	3.957	3.947	3.938	0.010	0.019	0.25	0.48	0.47

From the above it is clear that ethylidene-aniline is a good inhibitor and the treatment thereof either by heating alone or heating with sulphur, particularly the latter, causes greatly increased effectiveness thereof. Similar effectiveness can be obtained by heating the previously heat treated ethylidene-aniline with varying amounts of sulphur. Apparently a small amount of sulphur is sufficient to give the desirable properties to ethylidene-aniline as an increase in the amount of sulphur added thereto did not seem to have any increased effect on the inhibiting properties of the material.

I have found that reagents of the above type may be dissolved in various solvents of organic nature and the solution, although containing considerably less of the inhibitor, nevertheless has a high inhibiting value which is greater than the inhibiting value of the reagent alone. In the following table I have shown the effect of dissolving the reagent in solvents, from which it will be noted that the inhibiting value is very high:

Reagent "A" consists of ethylidene-aniline heated with 5% sulphur dissolved in an equal quantity of acetone and alcohol so that the reagent is ⅓ by weight of the solution.

Reagent "B" is the same substance dissolved in the same proportions of alcohol and chlorbenzol.

Reagent "C" is the same substance dissolved in the same amounts of alcohol and ethylidene di-chloride, and

Reagent "D" is the same amount of the same substance dissolved in alcohol and carbon tetrachloride.

It is highly desirable that the inhibitor be in solid granular form in order to avoid the necessity of placing the inhibitor in steel

containers for shipment. I have, therefore, made a large number of mixtures with various substances to determine whether such solid granular compositions easy to handle and readily effective as inhibitors could be made. Among such compositions which I have found effective is a mixture of a sulphur treated ethylidene-aniline with dry commercial soda ash (D—27) and a mixture of the same substance with soda ash and anhydrous sodium sulphate (D—36). The results obtained by the use of such mixtures is shown in the following table:

Reagent	Amount of reagent grams	Weight of metal grams			W grams		Per cent loss		Average per cent loss in 40 min.
		At start	After 20 min.	After 40 min.	20 min.	40 min.	20 min.	40 min.	
D-27	0.075	3.620	3.597	3.570	0.023	0.050	0.63	1.38	
	0.075	3.607	3.581	3.558	0.026	0.049	0.72	1.36	1.37
	0.375	3.580	3.572	3.568	0.008	0.012	0.22	0.33	
	0.375	3.426	3.417	3.410	0.009	0.016	0.26	0.47	0.40
D-36	0.100	4.112	4.091	4.067	0.021	0.045	0.51	1.10	
	0.100	3.970	3.950	3.927	0.020	0.043	0.50	1.10	1.10
	0.200	4.099	4.081	4.065	0.018	0.034	0.44	0.83	
	0.200	4.200	4.184	4.165	0.016	0.035	0.38	0.84	0.84
	0.400	4.131	4.120	4.108	0.011	0.023	0.27	0.56	
	0.400	4.213	4.202	4.185	0.011	0.028	0.26	0.66	0.61

I have further tested some of the above compositions in a pickling solution at a lower temperature than given above, namely, at 158° to 160° F. Under such conditions the results obtained were somewhat better than at the higher temperature, but in either case whether at the higher or the lower temperature the inhibiting value of my compounds approaches perfection, that is, there is substantially no loss of metal due to the action of the acid in the pickling solution.

Although I have described my invention with particular emphasis upon the ethylidene-aniline compositions, and have shown that the sulphur compounds thereof are highly effective as inhibitors, my invention is not limited to this class of substances as I have found that other groups of compounds of similar nature are also effective, particularly when heated with sulphur. In producing my compositions I may use in place of aniline, toluidine, xylidene or derivatives thereof, and in place of formaldehyde or acetaldehyde, I may use substances giving similar reactions. The amounts of inhibitor used in pickling baths may of course be varied widely and the figures contained herein are to be considered as merely illustrating the small amounts which may be effectively used. Although under different circumstances greater or lesser amounts might be used, I consider my invention to apply broadly to the use of aldehyde compounds of aromatic amines as such or modified by suitable treatment, and my invention is not to be limited except as set forth in the claims appended hereto.

The solvents for the inhibitors or the solid granular carrier materials previously described act in the nature of dispersing agents for the inhibitors in that they assist in dispersion of the inhibitor throughout the pickling bath, thereby increasing polymerization and inhibiting activity, in accordance with the well-known principles of colloid chemistry. Other dispersing agents than those mentioned may, of course, be used without departing from the spirit and scope of the invention.

What I claim is:

1. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a sulphurized aldehyde-aromatic amine compound.

2. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of an ethylidene-aniline compound.

3. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a sulphurized ethylidene-aniline compound.

4. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of an ethylidene-aniline compound which has been subjected to heat for a substantial period of time.

5. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a solution of an ethylidene-aniline compound.

6. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a solution of a sulphurized ethylidene-aniline compound.

7. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a mixture of an ethylidene-aniline compound with a solid dispersing agent.

8. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a mixture of a sulphurized ethylidene-aniline compound with a solid dispersing agent.

9. A method of pickling metals which com-

prises subjecting the same to a pickling bath containing a small amount of an ethylidene-aniline compound previously heated with about 5% to 15% sulphur.

10. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of an ethylidene-aniline compound previously heated with about 5% sulphur.

11. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of an aldehyde-aromatic amine compound and a dispersing agent for said compound.

12. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a sulphurized aldehyde-aromatic amine compound and a dispersing agent for said compound.

13. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of an ethylidene-aniline compound and a dispersing agent for said compound.

14. A method of pickling metals which comprises subjecting the same to a pickling bath containing a small amount of a sulphurized ethylidene-aniline compound and a dispersing agent for said compound.

In testimony whereof, I have hereunto subscribed my name this 25th day of June, 1929.

GEORGE BARSKY.