

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA JAGDISH BOSE ROAD,
CALCUTTA-17.

Specification No. 107414, 10th October 1966. Complete Specification left on 9th August 1967.

(Accepted 10th April 1968)

Index at acceptance—103[XLV(1)]

"IMPROVEMENT IN OR RELATING TO INHIBITION OF CORROSION DURING REMOVAL OF RUST AND
SCALE BY ACID SOLUTIONS"

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN
INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT
(ACT XXI OF 1860)

This is an invention by Kummattithidal Santhanam RAJAGOPALAN, Scientist, Narayanaswami SUBRAMANYAN,
Scientist and Meyyappa SUNDARAM, Senior Scientific Assistant-all of the Central Electrochemical
Research Institute, Karaikudi-3, India, all Indian citizens.

PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to improvements in or relating to
Corrosion Behaviour in Acid Solutions.

Hitherto it has been proposed that in the use of commonly available acids such as hydrochloric, sulphuric and phosphoric acids for removal of rust and scale from steel sheets and fabricated parts, the attack of steel base by the acid can be prevented by addition of what is known as a 'Corrosion Inhibitor'. A large number of acid inhibitors are known. In particular, it has been found that some in-organic compounds like arsenious and antimony oxides and organic compounds like amines and aldehydes possess a high degree of inhibition for steel in hydrochloric acid. Proteins and their hydrolysis products, heterocyclic compounds and alkaloids have been found to be effective inhibitors for steel in sulphuric acid.

This is open to the objection that the inhibitors so far used in acid solutions to prevent attack of steel while removing rust and scale are harmful to one or other of the non-ferrous metals, and some of the inhibitors which are effective in hydrochloric acid are much less effective in sulphuric acid.

The object of the present invention is to develop an inhibitor mixture which (1) would give a very high degree of inhibition to steel in both sulphuric and hydrochloric acids and (2) inhibits corrosion of other metals such as copper, zinc and aluminium.

The invention consists in the development of an inhibitive mixture which would give inhibition of corrosion in hydrochloric and sulphuric acids to a number of metals such as steel, zinc, copper and aluminium. Experiments carried out in this direction show that by an appropriate combina-

tion of anionic and cationic inhibitors, it is possible to get an inhibitive mixture which would give protection to steel, zinc, aluminium and copper in both hydrochloric and sulphuric acids. A mixture of a halide, a heterocyclic compound and a glucoside is found to give this result. Examples of halides are NaCl, NaBr, NaI, KCl, KBr and KI. Examples of heterocyclic compounds are pyridine, quinoline and piperidine. Examples of glucosides are tannins, vegetable gums etc.

The concentration ranges of the acid, inhibitor etc., for which the above invention applies are given below :

Concentration of acid	— 1 to 50%
halide	— 0.01 to 1%
heterocyclic compound	— 0.01 to 1%
glucoside	— 0.1 to 5%
Temperature	— 25° C to 80°C.

The performance of the inhibitor mixture is illustrated below :

Description of test :	Weighed metal specimen is suspended in 10% hydrochloric acid by means of glass hook for 1 hour at room temperature, after which it is taken out, washed, dried and weighed. The different in weight gives weight loss.
-----------------------	--

The inhibition efficiency is given by $W_1 - W_2 \times 100$ where W_1 is the weight loss without inhibitor and W_2 is the weight loss with inhibitor.

PERFORMANCE OF INHIBITOR MIXTURE

TABLE 1 (a)

Weight loss* in

Metal	10% HCl	10% HCl with Inhibitive Mixture	Inhibition Efficiency
	(in gms)	(in gms)	%
1. Mild Steel	0.4739	0.0063	98.6
2. Zinc	4.1883	0.133	96.6
3. Copper	0.0028	0.0025	10
4. Aluminium	0.0483	0.0063	87

*3" × 2" specimens were used.

Price : TWO RUPEES.

TABLE 1 (b)
Weight loss* in

Metal	10% H ₂ SO ₄	10% H ₂ SO ₄ with Inhibitor Mixture	Inhibition Efficiency
	(in gm)	(in gm)	%
1. Mild Steel	0.1673	0.0048	97.5
2. Zinc	04.022	0.0304	99.5
3. Copper	negligible	negligible	—
4. Aluminium	negligible	negligible	—

*2" × ½" specimens were used.

The following are among the main advantages of this invention :

- 1) The above-said inhibitor gives a very high degree of inhibition to steel during removal of rust and scale in commonly available acids such as hydrochloric acid and sulphuric acid.
- 2) The above-said inhibition mixture enables the use

of commonly available acids such as hydrochloric and sulphuric acids for removal of rust and scale from composite system containing both steel and one or more non-ferrous metals such as zinc, aluminum copper, brass etc.

- 3) The above said inhibitor mixture is equally effective in both sulphuric and hydrochloric acids.

COMPLETE

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This invention relates to improvement in or relating to inhibition of corrosion during acid cleaning of composite systems.

Hitherto it has been proposed that in the use of commonly available acids such as hydrochloric, sulphuric and phosphoric acids for removal of rust and scale from steel base by the acid can be prevented by addition of what is known as a 'Corrosion Inhibitor'. A large number of acid inhibitors are known. In particular, it has been found that some inorganic compounds like arsenious and antimony oxides and organic compounds like amines and aldehydes possess a high degree of inhibition for steel in hydrochloric acid. Proteins and their hydrolysis products, heterocyclic compounds and alkaloids have been found to be effective inhibitors for steel in sulphuric acid.

This is open to the objection that the inhibitors so far used in acid solutions to prevent attack of steel while removing rust and scale are harmful to one or other of the non-ferrous metals, and some of the inhibitors which are effective in hydrochloric acid are much less effective in sulphuric acid.

The object of the present invention is to develop an inhibitor mixture which (1) would give a very high degree of inhibition to steel in both sulphuric and hydrochloric acids and (2) inhibits corrosion of other metals such as copper, zinc and aluminium.

The inhibitor mixture developed prevents attack of both ferrous metals e.g., steel, and non-ferrous metals e.g., zinc, copper and aluminium during acid cleaning.

The inhibitor mixture makes it possible to clean free of rust and scale systems in which both ferrous and non-ferrous components are present.

The invention consists in the development of an inhibitive mixture which would give inhibition of corrosion in hydrochloric and sulphuric acids to a number of metals such as steel, zinc, copper and aluminium. Mixtures of (1) halide e.g., chloride, bromide, iodide, (2) heterocyclic compound e.g., pyridine, quinoline, piperidine and (3) glucosides e.g., tannins, vegetable gums are found to give this result.

The concentration ranges of the acid to be used, the constituents of the inhibitor mixture are given below :—

Concentration of acid	— 1 to 10%
Halide	— 0.01 to 1%
Heterocyclic compound	— 0.01 to 1%
Glucoside	— 0.01 to 5%
Temperature	— 25°C to 80°C.

Example 1

The following procedure may be followed to prepare one litre of inhibited 10% HCl solution. 0.5 grams of tannic acid is dissolved in 10 c.c.s. of distilled water. 1 gram of quinoline in the form of a solution, 10 c.c. of 10% HCl is added to the tannic acid solution, followed by 1.5 grams of potassium iodide. The solution thus obtained is now mixed with 1 litre of 10% HCl and stirred well.

Example 2

The following procedure may be followed to prepare one litre of inhibited 10% H₂SO₄ solution.

0.5 grams of tannic acid is dissolved in 10 c.c.s of distilled water, 1 gram of quinoline in the form of a solution, [10 c.c. of 10% HCl] is added to the tannic acid solution, followed by 1.5 grams of potassium iodide. The solution thus obtained is now mixed with 1 litre of 10% H₂SO₄ and stirred well.

The efficiencies of inhibitor for the two examples cited above are given in following Tables 1 and 2.

Description of Test :

5 cm. × 1.25 cm. abraded with 120 emery, degreased and weighed metal specimen is suspended in 10% hydrochloric acid by means of glass hook for 1 hour at room temperature, after which it is taken out, washed, dried and weighed. The difference in weight gives weight loss. The inhibition efficiency is given by $\frac{W_1 - W_2}{W_1} \times 100$, where W_1 is the weight loss in grams without inhibitor and W_2 is the weight loss in grams with inhibitor. In the experiments in sulphuric acid, the test is carried out at 60°C.

TABLE 1A
Efficiencies of inhibition for Example 1

Metal	Weight loss in HCl un-inhibited (gms.)	Weight loss in inhibited HCl as per example (gms.)	Inhibitor efficiency (%)
Mild Steel	0.0295	0.0038	80
Zinc	1.1081	0.0421	96
Copper	0.0007	Nil	100
Aluminium	0.03551	0.0069	81

TABLE 1B
Efficiencies of inhibition for example 1 when metals are coupled together:

Metal	Weight loss in HCl un-inhibited (in gms.)	Weight loss in inhibited HCl as per example 1 (in gms.)	Inhibitor (%)
1. Zinc (when coupled to mild steel of same area)	1.9839	0.2357	88
2. Mild Steel (when coupled to copper of same area)	0.1049	0.004	96

TABLE 2

Metal	Weight loss in H ₂ SO ₄ un-inhibited (gms.)	Weight loss in inhibited H ₂ SO ₄ as per example 2 (gms.)	Inhibitor (%)
Mild Steel	1.4848	0.0907	94
Zinc	5.9667	1.2358	80
Copper	Negligible	Negligible	—
Aluminium	Negligible	Negligible	—

The above-said inhibitor mixture gives a very high degree of inhibition to steel during removal of rust and scales in commonly available acids such as hydrochloric acid and sulphuric acid.

The above-said inhibitor mixture enables the use of commonly available acids such as hydrochloric acids for removal of rust and scale from composite system containing both steel and one or more non-ferrous metals such as zinc, aluminium, copper, brass etc.

The above-said inhibitor mixture is effective in both sulphuric and hydrochloric acids.

It has been shown that an inhibitor mixture prepared by mixing a halide, a glucoside and a heterocyclic compound can inhibit corrosion of both ferrous and non-ferrous metals during acid cleaning of composite systems :—

We claim :

1. An inhibitive mixture which would give inhibition of corrosion in hydrochloric and sulphuric acids to a number of metals such as steel, zinc, copper and

aluminium which comprises mixtures of (1) halide e.g., chloride, bromide, iodide, (2) heterocyclic compound e.g., pyridine, quinoline, piperidine and (3) glucosides e.g., tannins, vegetable gums.

2. An inhibitive mixture as claimed in claim 1 when employed to give inhibition over an acid concentration range of 1 to 10%.
3. An inhibitive mixture as claimed in claim 1 when employed to give inhibition over a temperature range of 25°C to 80°C.
4. An inhibitor mixture as claimed in claim 1 when used to prevent metal attack during acid cleaning of systems having both ferrous and non-ferrous parts.

Dated this 7th day of August, 1967.

Sd.

PATENTS OFFICER

Council of Scientific and Industrial Research.