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 CALCUTTA-17.**

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"A NEW FORMULATION OF PICKLING INHIBITORS FOR STEEL IN ACID SOLUTIONS"

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 INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION
 OF SOCIETIES ACT (ACT XXI OF 1860).**

**This is an invention (1) Narayanaswamy Subramanyan, Scientist, (2) Serukai Krishnamachari Rangarajan,
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 Assistant, all of the Central Electrochemical Research Institute,
 Karaikudi-3 Tamil Nadu, India, all Indians.**

PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to a new formulation of pickling inhibitors for steel in acid solutions.

Hitherto it has been the practice to employ as inhibitors various materials to prevent the loss of metal, when steel is pickled in mineral acids.

This is open to the objection that steel when pickled in mineral acid may become brittle because of the uptake of hydrogen generated during pickling.

The object of this invention is to formulate inhibitor-compositions which give high inhibition efficiency in pickling steel and at the same time effectively minimise the uptake of hydrogen.

To these ends, the invention broadly consists in combining in suitable proportions:

- (a) a substance or a mixture of substances containing sulphur (thiourea and its derivatives, other organic sulphides etc) which is effective as corrosion inhibitor for steel in acid solutions, and
- (b) a substance or a mixture of substances containing oxygen or nitrogen with carbon and hydrogen (amines, aldehydes etc) which has the special quality of minimising the permeation of hydrogen into the metal during pickling.

The following are the typical examples of the invention:

TABLE 1

Percentage inhibition efficiency and hydrogen permeation current in presence of inhibitors for steel in 0.5N HCl

S. No.	Inhibitor	Percentage inhibition efficiency	Hydrogen permeation μA
1		..	5.8
2	10 mM thiourea	85.0	13.0 increases with time
3	10 mM thiourea + 0.03% HCHO	92.0	1.5
4	10 mM thiourea + 0.05% hexamine	95.0	1.6
5	Formaldehyde 2.0%	95	3.6
6	Hexamine 0.1%	94	3.2

Price : TWO RUPEES.

TABLE 2

Percentage inhibition efficiency and hydrogen permeation current in presence of inhibitors in higher acid concentrations

S. No.	Inhibition	Acid concentration	Percentage inhibition efficiency	Hydrogen permeation current A/ μ
1		5N.HCl		44
2	10 mM thiourea	5N.HCl	88	41
3	10 mM thiourea + 0.6% formaldehyde	5N.HCl	98	9
4	10 mM thiourea + 0.05% hexamine	5N.HCl	91	24
5		2N.H ₂ SO ₄	..	38
6	10 mM thiourea	"	92	6
7	10 mM thiourea + 0.6% formaldehyde		92	5

The following is the main advantage of the invention:

1. With a low inclusion of hydrogen into the metal, the possibility of hydrogen embrittlement during acid

pickling of steel is decreased by using this combination of substances, in addition to obtaining a high degree of corrosion inhibition.

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 a process of formulating corrosion-inhibiting compositions and the formulation of a new type of pickling inhibitors for steel in acid solutions, which finds applications in metal finishing processes.

Hitherto it has been the practice to employ as inhibitors various materials like formaldehyde, hexamine and thiourea to prevent the loss of metal when steel is pickled in mineral acids.

This is open to the objection that steel when pickled in mineral acid containing the corrosion inhibitors may become brittle because of the uptake of hydrogen generated during pickling.

The object of this invention is to formulate inhibitor-compositions which give high inhibition efficiency in pick-

The proportion of the constituents are:

Thiourea	0.001 to 1.10%
Formaldehyde	0.10 to 1.0%
Hexamine	0.01 to 0.10%

The invention includes within its scope a process of pickling steel items in mineral acid solutions containing corrosion inhibitors prepared as defined herein.

The preferred proportions are :

Thiourea	0.002 to 0.03%
Formaldehyde	0.2 to 0.8%
Hexamine	0.02 to 0.08%

The addition of mixtures of corrosion inhibitors and substances which effectively reduce the uptake of hydrogen by the metal to pickling acids is helpful in reducing the absorption of hydrogen by the metal and minimising the possibility of hydrogen embrittlement.

Tables 1 and 2 bring out the merit of the invention in quantitative terms.

TABLE 1

Percentage inhibition efficiency and hydrogen permeation current in presence of inhibitors for steel in 0.5M HCl

Temperature of pickling = $30 \pm 2^\circ\text{C}$

S. No.	Inhibitor	Percentage inhibition efficiency	Hydrogen permeation μA
1	5.8
2	0.08% thiourea	85.0	13.0 (increases with time)
3	0.08% thiourea + 0.03% formaldehyde	92.0	1.5
4	0.08% thiourea + 0.05% Hexamine	95.0	1.6
5	Formaldehyde 2.0%	95	3.6
6	Hexamine 0.1%	94	3.2

TABLE 2

Percentage inhibition efficiency and hydrogen permeation current in presence of inhibitors in higher acid concentrations

Temperature of pickling = $30 \pm 2^\circ\text{C}$

S. No.	Inhibitor	Acid concentration	Percentage inhibition efficiency	Hydrogen permeation current A#
1	...	5M. HCl	...	44
2	0.08% thiourea	5M. HCl	88	41
3	0.08% thiourea + 0.6% formal	5M. HCl	98	9
4	0.08% thiourea + 0.05% hexamine	5M. HCl	91	24
5	...	1M. H ₂ SO ₄	...	38
6	0.08% thiourea	-do-	92	6
7	0.08% thiourea + 0.6% formaldehyde	-do-	92	5

The present invention consists of a process which comprises pickling steel items in mineral acid solutions containing corrosion inhibitors wherein suitable combinations of these substances are employed to get good corrosion inhibition and reduced hydrogen uptake thereby minimising the possibility of hydrogen embrittlement.

The following is the main advantage of the invention:

With a low inclusion of hydrogen into the metal, the possibility of hydrogen embrittlement, during acid pickling of steel is decreased by using this combination of substances, in addition to obtaining a high degree of corrosion inhibition.

The invention consists of a process of reducing hydrogen uptake during pickling of steel items in acid solutions by the addition of suitable combinations of corrosion inhibitors to the acid solutions whereas individual substances do not either affect the hydrogen uptake or reduce it considerably.

We claim:

1. A process of formulating corrosion-inhibitive compositions useful in pickling steel items in commercial acid solutions, characterised in that suitable proportions of the following are combined (a) substances containing sulphur (for example thiourea and its derivatives or other organic sulphides) which are effective as corrosion-inhibitors and (b) substances containing oxygen or nitrogen with carbon and hydrogen (for exa-

mple amines and aldehydes) which have the special characteristic of minimising the permeation of hydrogen into the metal during pickling.

2. A process as claimed in claim 1, wherein thiourea, formaldehyde and hexamine are combined to give a corrosion-inhibitive formulation and added to mineral acid used for pickling steel items.
3. A process as claimed in claims 1 and 2, wherein the proportion of the constituents are:

Thiourea	0.001 to 0.10%
Formaldehyde	0.10 to 1.0%
Hexamine	0.01 to 0.10%
4. A process of formulating corrosion-inhibitive compositions for use in pickling steel items in commercial acid solution as claimed in claims 1, 2 and 3.

Dated this 22nd day of October 1971.

Sd.

PATENTS OFFICER

Council of Scientific & Industrial Research