Government of India, The Patent Office, 214, Acharya Jagadish Bose Road, Calcutta- 17. Complete specification No.132142 dated 22nd September 1975. Application and Provisional specification No.1532/Cal/1974 dated 9th July 1974.

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International classification- C23f 11/00, 15/00, F16 1 59/00

"IMPROVEMENTS IN OR HELATING TO INHIBITION OF CORROSIDN

OF STEEL IN COOLING WATER SYSTEMS"

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 1960).

The following specification describe the nature of this invention:-

This is an invention by Dr. NARAYANASWAMI SUBRAMANYAN, Scientist, KHISHRASWAMI BALAKRISHNAN, Scientist, BHAGAVATHI SATHIANAN. DHAM, Senior Scientific Assistant and MAHADEVA IYER KRISHNAN, Junior Scientific Assistant all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India. all Indian citizens.

PRICE Re.2/-

This invention relates to improvements in or relating to the inhibition of corrosion of steel in cooling water systems.

phosphates
Hitherto it has been proposed that chromates and silicates
alone or in combination are used as corrosion inhibitors for
steel in cooling water, particularly in recirculating systems.

This is open to the objection that chromates at concentrations generally employed (300-500 ppm) are toxic from the
point of view of disposal and can give rise to dangerous
localised corrosion, if used singly at lower concentrations.
The chromate-phosphate combination can facilitate scale
formation and also cause corrosion of any copper components
in the cooling system, apart from favouring bacterial growth.
Gilicates are used in high conentrations.(3000-4000 ppm).

The object of this invention is to obviate these disadvantages by avoiding the use of chromates and phosphates and employing relatively lower concentrations of silicate.

To these ends, the invention broadly consists in combining silicate with organic amines like cyclohexyl amine, morpholine or triethanol amine and sodium citrate in the following ranges of concentrations, including benzotriazole (2 to 10 ppm) to take care of possible attack of copper or brass componnents wherever necessary.

Silicate : 250-1500 ppm

: 100-500 ppm Amine

Trisodium Citrate: 100-500 ppm

Though these chemicals are known to be corrosion inhibitors they do not give a high degree of inhibition. except at high concentrations in water containing chloride ions as is evident from Table 1.

TABLE 1

	Solution - 10 ppm NaCl Tem	$p. = 30 \pm 2^{\circ}C$
	Mild steel of size 3" x 1"	
8.No.	Inhibitor ppm	I.E.(%) for 10 days
1.	Triethanol amine (250)	51
2.	TRA 250 + sodium citrate 250	60
3•	TRA (250) + sodium silicate(250)	42
4.	Sodium silicate (250) + sodium citrate(250)	52

sodium citrate(250)

Morpholine (1000)

5.

A suitable combination of these substances however can give a high degree of inhibition at comparatively lower concentrations under similar circumstances. This is brought out in examples I to III given below:

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Temp. = $30 \pm 2^{\circ}C$

Solution = 10 ppm MaCl

Mild steel of size = 3" x 1"

Inhibitive combination (in ppm)	I.B.(%) for 10 days	I.B.(%) for 30 days
1) T.E.A. (250) + Sodium citrate (250) + Sodium silicate (250)	99.9	68
2) T.B.A. (100). + Sodium citrate (100) + Sodium silicate (500)	100	74
3) T.B.A. (100) + Sodium citrate (500) + Sodium silicate (500)	100	99
4) T.B.A.(500) + Sodium citrate(500) + Sodium silicate(500)	100	95
5) Morpholine (250) + Sodium citrate (250) +Sodium silicate (250)	100	95
6) Morpholine(250) + Citrate (250) + Silicate(250) + Benzatriazole(10)		100
<pre>7) Morpholine(500) + Sodium citrate(500) + Sodium silicate(500)</pre>	100	100
8) Cyclohexyl amine (100) + Sodium citrate (500) + Sodium silicate(500)	100	96
Duration: 1	C solution = 100 0 days f size 3" x 1"	ppm NaCl
	<u>Inhibi</u>	tion effectency(%)
1) T.B.A. (100) + Sodium silicate(500) + Sodium citrate (500)		73
2) Cyclohexylamine (100) + Bodium silicate (500) + Sodium citrate (500)	,	73
3) Morpholine (100) + Sodium silicate (500) * Sodium citrate (500)		83

Example 13

Temp. = 80 ± 5°C

Duration = 10 days

Mild steel of size 3" x 1"

Inhibition efficiency (%)

	10 ppm NaCl	100 ppm Nacl	
1) T.E.A. (100) + Sodium citrate (500) + Sodium silicate(500)	100	A few rust spots	
2) Morpholins (100) + Sodium citrate (500) + Sodium silicate(500)	100	do	
3) Cyclohexylamine (100) + Sodium citrate (500) + Sodium silicate(500)	100	do	
Example: 4	•		
Metal = Copper 3" x	1" Solution	1" Solution = 10 ppm NaCl	
Duration = 30 days	Temp. 30	Temp. 30 + 2°C	
Inhibitor combination	Weight (m.g		
1) Control	2.	4	
2) T.E.A. (100) + Sodium silicate (500) + Sodium citrate (500)	3.	3	
<pre>3) Combination (2) + Benzotriazole (2 ppm)</pre>	2.	7	
4) Morpholine (250) + Sodium citrate (250) + Sodium silicate (250) + Benzotriazole (10 ppm)	ni	1	
5) Morpholine (100) + Sodium citrate (500) + Sodium silicate(500) + Benzotriazole(10)	in	1	
6) Cyclohexylamine (250) + Sodium citrate (250) + Sodium silicate (250) + Benzotriazole (10)	n.i.	.1	

The following are among the main advantages of the invention:

- 1) It is possible to avoid completely the use of toxic substances like chromates in inhibiting the corrosion of steel in cooling water systems.
- 2)Even without chromate, a high degree of corrosion inhibition is achieved by suitable combination of amine, silicate and citrate.
- 3) The incorporation of benzotriazole in the inhibition combination makes it harmless to copper components in the system.
- 4) Pollution problem is considerably minimised by the avoidance of toxic chemicals.

Dated this 2nd day of July, \$974

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Asstt.Patents Officer,
Council of Scientific & Industrial Resear-

THE PATENT ACT 1970

COMPLETE SECTION SECTION 10

IMPROVEMENTS IN CARROLLING TO INHIBITION OF CORROSION OF STEEL IN COULING WATER SYSTEMS.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body rorm incorporated under the Registration of Societies act (Act XXI of 1860).

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The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:-

This is an invention by Dr. Narayanaswami Subramanyan, Scientist, Dr. Krishnaswami Balakrishnan, Scientist, Sri Bhagavathi Sathianandham, Senior Scientific Assistant, and Sri Mahadeva Iyer Krishnan, Junior Scientific Assistant all of Central Electrochemical Research Institute, Karaikudi-6, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to the inhibition of corrosion of steel in cooling water systems.

Hither_to it has been proposed that chromate, phosphetes and silicates, alone or in combination are used as corrosion inhibitors for steel in cooling water, particularly in recirculating systems.

This is open to the objection that chromates at concentrations generally employed (300 - 500 ppm) are toxic from the point of view of disposal and can give rise to dengarous localised corrosion, if used singly at lower concentrations. The chromate-phosphate combination can facilitate scals formation. High concentration of phosphates can, in addition, cause corrosion of any copper components in the cooling system, while phosphate alone can favour bacterial growth. Silicates are used in high concentrations of the order of 3000 to 4000 ppm in water containing chloride basis.

The object of this invention is to obviate these disadvantages by avoiding the use of chromates and phosphates and employing falative by lower concentrations of silicate.

(1)	(2)	(3)

7 7rs /4nh\		
3. TEA (100)		
+ Sodium citrate (500)		
+ Sodium silicate (500)	100	99
4. TEA (500)		
+ Sodium oitrate (500)		
+ Sodium silicate (500)	100	95
5. RRA Morpholine (250)		
+ Sodium citrate (250)	4.00	
+ Sodium milicate (250)	100	95
6. Morpholine (250)		
+ Sadium citrate (250)		
+ Sedium silicate (250)		
+ Benzotriazole (10)	100	100
7. Morpholine (500)		
+ Sedium citrate (500)		
+ Sedium ellicate (SOC)	100	100
	, 33	
8. Cyclohexyl amine (100)		
+ Sedium citrate (500)	4 **	~
+ Sodium Silicate (500)	100	96
Committee Co		
Example 21		
Mild Steel and	cimens of eize 3" x 1"	
		m NaCl
Temperature : 30 ± 2°C ::	2010cton 1 inc bb	M 11604
Duration	10 days	
	Inhibition Efficie	nev (%)
	Inhibition Efficie	noy (%)
4 TC4 [400)	Inhibition Efficie	ngy (%)
1. TEA [100)	Inhibition Efficie	nay (%)
+ Sodium silicate (500)	Inhibition Efficie	ngy (%)
+ Sodium silicate (500) + Sodium oitrate (500)		ngy (\$)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800)		ngy (\$)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500)	73	ngy (%)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800)		ngy (%)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500)	73	<u>noy (≴)</u>
+ Sodium silicate (500) + Sedium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500)	73	<u>noy (≴)</u>
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500)	73	<u>ngy (≴)</u>
+ Sodium silicate (500) + Sedium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500)	73	ngy (%)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500)	73	ngy (%)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium citrate (500) + Sodium citrate (500)	73 73 83	ngy (%)
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500)	73 73 83	
+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (300) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime	73 73 83	
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (300) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime	73 73 83 ns of size 3" x 1" 88 Duration 8 25 0	iaya*
+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (300) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime	73 73 83 83 83 18 of size 3" x 1" 11 Duration 1 25 6 Inhibition efficiency	daya*
+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (300) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime	73 73 83 ns of size 3" x 1" 88 Duration 8 25 0	daya*
+ Sodium silicate (500) + Sedium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C	73 73 83 83 83 18 of size 3" x 1" 11 Duration 1 25 6 Inhibition efficiency	daya*
+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C	73 73 83 83 83 18 Ouration 8 25 6 Inhibition afficiency 10 ppm NeCl 100 ppm 9	daya*
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+ Sodium silicate (500) + Sodium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Merpholine (100)	73 73 83 83 83 Ins of size 3" x 1" 11 Ouration : 25 c Inhibition efficiency 10 ppm NeCl 100 ppm 1	days* (<u>\$)</u> laC1
+ Sodium silicate (500) + Sodium oitrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500)	73 73 83 83 83 18 Ouration 8 25 6 Inhibition afficiency 10 ppm NeCl 100 ppm 9	daya*
+ Sodium silicate (500) + Sedium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500)	73 73 83 83 83 Ins of size 3" x 1" 11 Ouration : 25 c Inhibition efficiency 10 ppm NeCl 100 ppm 1	days* (<u>\$)</u> laC1
+ Sodium silicate (500) + Sedium citrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500) S. Cyclohexylamine (100)	73 73 83 ns of size 3" x 1" 11 Ouration 1 25 6 Inhibition sfficiency 10 ppm NeCl 100 ppm F 98 97	days* (<u>\$)</u> laC1
+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500) 5. Cyclohexylamine (100) + Sodium citrate (500)	73 73 83 83 83 Ins of size 3" x 1" 11 Ouration : 25 c Inhibition efficiency 10 ppm NeCl 100 ppm 1	days* (<u>\$)</u> laC1
+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500) 5. Cyclohexylamine (100) + Sodium citrate (500) 1. Tex (500)	73 73 83 83 ns of size 3" x 1" 11 Duration : 25 c Inhibition sfficiency 10 ppm NaCl 100 ppm 9 98 97 98 81	daye* (<u>\$)</u> (aC1
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+ Sodium silicate (500) + Sedium oitrate (500) 2. Cyclohexylamine (800) + Sodium silicate (500) + Sodium citrate (500) 3. Morpholine (100) + Sodium silicate (500) + Sodium citrate (500) Example 3: Mild Steel specime Temperature : 80 ± 5°C 1. TEA (100) + Sodium citrate (500) 2. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500) 5. Cyclohexylamine (100) + Sodium citrate (500)	73 73 83 83 83 11 Ouration 1 25 6 Inhibition efficiency 10 ppm NeCl 100 ppm 9 98 97 98 91 99 98	days* (5) (6C) 30

Exemple 48

Copper Specimen of edge 30 x 46

Sclution a 40 ppm NaCl as Duration a 30 days

Inhibiter combination	1381 389 460 A4 600 388 460 460	ਫ਼ ਬੜੇ /ਚ ਕੜੇ ਆਪਣੇ ਬੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕੜੇ ਕ	Weight loss (m.gmt)
1. Control			2,4
2. TEA (100) + Sodium silicate (500) + Sodium citrate (500)			3.3
3. Combination (2) + Benzotriazole (2 ppm)			2.7
4. Morpholine (250) + Sodium citrate (250) + Sodium silicate (250) + Benzotriezole (10 ppm)			n 1. 1
5. Morpholine (100) + Sodium citrate (500) + Sodium silicate (500) + Benzotriazole (10)			nil
6. Cyclohexylamine (250) + Sodium citrate (250) + Sodium eilicate (250) + Benzotriazole (10)		and the control of th	

The following are smong the main advantages of the invention:

- 1. It is possible to avoid complately the use of toxic substances like chromate in inhibiting the corrosion of steel in cooling water systems.
- 2. Inhibition of corrosion of steel greater than 90% for more than 30 days is obtained by any of the above mentioned combinations.
- 3. The incorporation of benzotriazols in the inhibitor combination makes it harmless to copper components in the system.
- 4. Pollution problem is considerably minimised by eliminating chromate.
 We claim:
- 1. A composition for inhibition of corrosion of steel in cooling water system comprising a combination of silicate, alignatic amines like cyclohexylemine and kakekak triethanolamine and salts of polycarboxyliq. organic acids like citric acid with or without benzotriazole in the



concentration ranges of amine 50 to 250 ppm, silicate 250 to 500 ppm and citrate 250 to 500 ppm.

- 2. A composition as claimed in claim (1) in water containing chloride up to a concentration of 100 ppm and up to a temperature of 80° C.
- 3. A composition for inhibition of corrosion of steel in cooling water systems substantially as herein before described.

Dated this 20th day of September 1975

GIPPP/(G.P & D.C.I)/79-80/150

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