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IMPROVEMENTS IN OR RELATING TO INHIBITION OF CORROSION OF METALS 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 1860).

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 KUMMAITITHIDAI SANTHANAM RAJACOPALAN, Scientist, and VENU (MRS), Scientist, both of the Central Electrochemcal research Institute, Karaikudi, Tamil Nadu, India, both Indian citizens.

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

Hitherto it has been proposed that (i) sodium hexameta phosphate, sodium chromates or sodium silicate can be used for inhibition of corrosion in once-through cooling water systems and (ii) sodium hexameta phosphate functions more effectively in presence of calcium.

This is open to the objection that (i) sodium hexameta phosphate by itself or in combination with calcium is not effective at various salt concentrations present in cooling waters, (ii)the specific concentrations of the cations and the ratios in which the constituents of a mixed inhibitor can be used are not known.

The main object of this invention is therefore to obviate these disadvantages by providing a mixed inhibitor formulations having specific concentrations of sodium hexameta phosphate, calcium oxide, magnesium sulphate, zinc sulphate, calcium chloride, which can give effective inhibition to variety of metals used in cooling systems and wide variations in the composition of cooling waters.

The main finding of the invention is that poly phosphates, calcium salt, magnesium salt, zinc salt and borax when mixed in powder form or in liquid form in specific concentrations and added in cooling waters - soft water containing high chloride and sulphate or soft water containing low chloride and sulphate effectively reduces corrosion of mild steel, copper, brass and aluminium in such cooling waters.

The result is that the variety of metals used in cooling water systems can be effectively protected against corrosion due to cooling waters of widely varying compositions which is not possible in the hitherto known processes.

According to the present invention, there is provided a process for inhibiting corrosion of metals in cooling water systems by i) preparing an inhibitor formulation using sodium hexameta phosphate and ii) adding the inhibitor to the cooling water characterised in that (i) the inhibitor formulation is prepared by combining the following constituents in the specified concentrations, namely, (a) combining sodium hexameta phosphate, borax, zinc sulphate and magnesium sulphate and calcium oxide in the ratio 2:1:1:1:1 by weight and grinding the above mixture to get a uniform powder product; or (b) dissolving 30 g of calcium chloride in 100 cc of distilled water to form pack No. 1, dissolving 4 g of borax and 20 g of sodium hexameta phosphate in 100 cc of distilled water to form pack No. II and dissolving 50 g of magnesium sulphate, 44 g of zinc sulphate and 42 g of magnesium chloride in 100 cc of distilled water to form pack No. III, and (ii) adding the inhibitor to the cooling water in the following concentration range, namely,

powder mixture:		250-750 ppm
or		
3 pack liquid	(1)	0.025 - 0.075 cc/l
	(2)	0.5 - 1.5 cc/l
concentrate	(3)	0.025 -0.15 cc/l.

The cooling waters may contain a wide variation in chloride (80-900 ppm) and sulphate (25-135 ppm) concentration.

The cooling water system may contain a variety of metals (mild steel, copper, brass and aluminium).

The process involves preparing a powder mix or liquid concentration of poly phosphates, calcium

salt, magnesium salt, zinc salt and borax in specific concentrations and adding the same in cooling waters which prevents the corrosion of variety of metals - mild steel, copper, brass, aluminium used in cooling water systems.

The following typical examples are given to illustrate the invention:-

Powder mix:	Polyphosphate	35 to 40 per cent weight
	Borax	15 to 25 "
	CaO	0 to 20 "
	$MgSO_4$	15 to 25 "
	$ZnSO_4$	0 to 20 "
Liquid concentrate:		
	Polyphosphate	15 to 25 per cent weight/volume
	Borax	3 to 5 "
	$CaCl_2$	25 to 35 "
	$MgCl_2$	40 to 45 "
	$MgSO_4$	45 to 55 "
	$ZnSO_4$	40 to 45 "

Table 1

Inhibitor for Natural Waters:

Type of Inhibitor	Constituents 1	2	3	4	5
Example I (powder)	$(NaPO_3)_6$	$Na_2B_4O_7.10\ H_2O$	CaO	$MgSO_4.7H_2O$	
Example II(powder)	"	"	"	"	
Example III(powder)	"	"	-	"	
Example IV A 3-pack liquid concentrate*					
(1)	$CaCl_2$	-	-	-	
(2)	$(NaPO_3)_6$ +	$Na_2B_4O_7.10\ H_2O$	-	-	
(3)	$MgCl_2.6H_2O$ +	$MgSO_4.7H_2O$ +	$ZnSO_4.7\ H_2O$	-	

N.B:- All chemicals used were L.R. grade.

The liquid concentrate is in the form of three separate packs which are individually added to the water in the dosages mentioned.

The concentration ranges in which the inhibitor is added to the cooling water are indicated below:-

Powder mixture:		250-750 ppm.
3 pack liquid Concentrate	(1)	0.025 - 0.075 cc/l
	(2)	0.5 - 1.5 cc/l
	(3)	0.025 - 0.15 cc/l

The performance of the above mentioned inhibitors is illustrated in the following examples:-

Example 1:

The data given in Tables 2 and 3 show that there is considerable decrease in corrosion rates of steel, copper, brass and aluminium in presence of the inhibitor both at room temperature as well as when heated to 80-85°C.

Example 2:

The performance of the 3-pack liquid concentrate is compared with a commercial product in Table 4.

Table 2

Corrosion rate of steel in unstirred solution at room temperature by total immersion of 2" x 1/2" panels in triplicate in a 250 c.c.beaker:

Solution	Test period (days)	Corrosion rate, mdd
5% Sea Water*	25	17.15 ± 0.65
5% Sea Water + 200 ppm $(NaPO_3)_6$	15	3.85 ± 0.25
5% Sea Water + 200 ppm $(NaPO_3)_6$ + 100 ppm Zn (as $ZnSO_4$)	15	2.1 ± 0.1
5% Sea Water + 200 ppm $(NaPO_3)_6$ + 100 ppm Ca^{2+} (as $Ca(NO_3)_2$)	15	2.7 ± 0.2
5% Sea Water + 200 ppm $(NaPO_3)_6$ + 100 ppm Ca^{2+} + 50 ppm Borax	15	0.5
5% Sea Water + 500 ppm Example No.I	20	2.5 ± 1.5
5% Sea Water + 500 ppm Example No.II	20	2.85 ± 0.55
Tap Water**	21	19.15 ± 3.15
Tap Water + 500 ppm Example No.I	20	1.5 ± 1.3
Tap Water + 500 ppm Example No.II	20	2.55 ± 1.25
Tap Water + 500 ppm Example No.III	30	0.95 ± 0.05

*Cl^- : 911, SO_4^{--} : 135; Mg^{++} : 60; Ca^{++} :: 22 (ppm)

**Cl^- : 81; SO_4 : 25; Mg^{++} : 15; Ca^{++} :: 47 (ppm)

TABLE 3

Corrosion rate of steel, copper, brass and Aluminium in unstirred solution by total immersion of 2" x 1/2" panels in 250 c.c. beaker for 30 days: (1) All the four panels in the same solution but not electrically connected. (Experiment in duplicate) and (2) Each separately in triplicate. Inhibitor : 500 ppm of Example No. III.

Material:	Corrosion rate in mdd (at room temperature)			Corrosion rate in mdd (when heated to 80-85°C for 99 hrs.,).		
	Tap Water	Tap water + Inhibitor	Distilled water + Inhibitor	Tap Water + inhibitor	Distilled water + inhibitor	Tap water + Inhibitor
Mild Steel	18.75±0.05 (rusted)	2.9 ± 0.3 (Interference film & spots)	11.75 ± 4.65 rusted	0.95 ± 0.05 (Interference film & spots)	35.5 ± 1.0 (rusted)	0.85 ± 0.25 Interference film and spots).
Copper	1.3 (violet film)	0.15 ± 0.04 (Bright)	0.3 (Tarnished)	0.15 ± 0.05 (tarnished)	0.35 ± 0.15 (tarnished)	0.55 ± 0.05 (Tarnished & violet pa
Brass	1.35 ±0.05 (violet film)	0.11 (Bright)	0.5 (Tarnished & tiny spots)	0.15 ± 0.05 (Tarnished & a few spots)	0.6 ± 0.1 (tarnished)	0.35 ± 0.15 (Tarnished and violet patches).
Aluminium	2.1 (Dulled & spots)	0.85 (Spots on edges)	0.7 ± 0.2 (Spots on edges)	0.3 (Spots on edges)	0.55 ± 0.15 (Spots on edges)	0.15 ± 0.05 (Spots on edges)

Table 4

Corrosion rate of mild steel in unstirred solution by total immersion of 2"x1/2" panels in triplicate in 250 c.c. beaker.

Solution	(Test period (days)	Corrosion rate, mdd at room temperature	Corrosion rate, mdd when heated to 80-85°C.
Tap water		19.15 ± 3.15	23.3 ± 0.4
Tap water + 0.04 cc/l, Aqua clear		17.95 ± 1.05	20.7 ± 1.9
Tap water + 1.5 cc/l, Aqua clear	21*	8.0 ± 1.9	20.25 ± 0.95
Tap water + 2 cc/l,, Aqua clear		5.2 ± 1.7	4.3 ± 1.0
Tap water + 3 cc/l, Aqua clear		5.75 ± 1.45	0.5 ± 0.3
Tap water + Example No.IV in cc/l., for each of the three components of the three pack system are given below:			
1 2 3		-	-
0.025 1.0 0.025		0.19 ± 0.1	0.85 ± 0.28
0.05 1.0 0.05	30**	0.19 ± 0.1	0.8 ± 0.18
0.05 1.0 0.125		0.22 ± 0.03	0.81 ± 0.14
0.025 1.0 0.125		0.20 ± 0.06	2.05 ± 0.73

* Total period at 80-85°C : 52 hours

** Total period at 80-85°C : 78 "

Table 5

Comparison of cost between a commercial product and the newly developed products for treating 1000 gallons of cooling water.

Inhibitor	Cost Rs. p
Aqua clear	15.00 (approx.,)
Example No. III	7.04
Example No. IV	6.75

Noteworthy Features

1. An effective inhibitor formulation having specific concentration of polyphosphates, calcium salt, magnesium salt, zinc salt and borax for preventation of corrosion in cooling water systems.
2. The inhibitor formulation is equally effective in cooling waters containing a wide variation in chloride (80-900 ppm) and sulphate (25-135 ppm) concentration.
3. The inhibitor formulation is equally effective whether used in powder form or in liquid form in specific concentrations.
4. The inhibitor formulation can prevent corrosion of variety of metals (mild steel, copper, brases and aluminium) used in cooling water systems.

We claim:-

1. A process for inhibiting corrosion of metals in cooling water systems by i) preparing an inhibitor formulation using sodium hexameta phosphate and ii) adding the inhibitor to the cooling water characterised in that (i) the inhibitor formulation is prepared by combining the following constituents in the specified concentrations, namely, (a) combining sodium hexameta phosphate, borax, zinc sulphate, magnesium sulphate and calcium oxide in the ratio 2:1:1:1: by weight and grinding the above mixture to get a uniform powder product; or (b) dissolving 30 g of calcium chloride in 100 cc of distilled water to form pack No.I, dissolving 4 g of borax and 20 g of sodium hexameta phosphate in 100 cc of distilled water to form pack No.II and dissolving 50 g of magnesium sulphate, 44 g of zinc sulphate and 42 g of magnesium chloride in 100 cc of distilled water to form pack No.III, and (ii) adding the inhibitor to the cooling water in the following concentration range, namely,

powder mixture:		250-750 ppm.
or-		
3 pack liquid concentrate	(1)	0.025 - 0.075 cc/l
	(2)	0.5 - 1.5 cc/l
	(3)	0.025 - 0.15 cc/l.

2. A process as claimed in claim 1 wherein the cooling waters contain a wide variation in chloride (80-900 ppm) and sulphate (25-135 ppm) concentration.

3. A process as claimed in claim 1 or 2 wherein cooling water system contain a variety of metals (mild steel, copper, brass and aluminium).

4. A process for inhibiting corrosion in cooling water systems substantially as herein before described.

Dated this 12th day of December, 1973.

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