

Water thinned shellac primer for steel effect of corrosion inhibitors

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A WATER thinnable anti-corrosive primer based on dewaxed lac and maleinised linseed oil had been developed earlier. The effect of incorporating six well known corrosion inhibitors namely potassium chromate, sodium chromate, strontium chromate, sodium nitrite, sodium benzoate and n-butylamine into this primer has now been investigated with the object of improving still further the anti-corrosive properties. Of these n-butylamine (0.1 per cent on the vehicle) has been found to give the best results improving both the mechanical and anti-corrosive properties. This composition on baking gives hard, adherent and elastic films with good resistance to corrosion and to the action of water, solvents and chemicals etc.

In view of its good mechanical and anti-corrosive properties the use of this primer is indicated in industries fabricating steel equipments and structures.

WATER THINNED primers are the latest developments in the field of surface coatings. These primers have gained importance due largely to the development of plastic emulsions and water soluble synthetic polymers.¹ Being water based these primers have several advantages, particularly freedom from fire risks and pollution of atmosphere,² ease of application and low cost of production.

In more advanced countries very successful compositions of water thinnable finishes particularly primers based on water soluble/dispersible resins have been developed and are being increasingly used in the automobile industry. These have gained further importance due to the recent development of electrodeposition technique for water thinned pigmented coatings.

In our country also some water soluble synthetic resins have been developed and are being manufactured but so far none of them has been used in such formulations. Amongst natural resin shellac has recently been used in the production of water thinned lacquers⁴⁻⁶ and primers⁷⁻¹⁰.

Chemical structure of this natural resin shows a close parance with the structure and mechanism of modern water soluble resins. Owing to the presence of one free carboxyl group in the molecule it dissolves freely in aqueous alkalis and organic bases to form clear varnishes. These aqueous varnishes do not adhere well on metals, glass etc. but when modified with, water soluble drying oils^{7,8} or self dispersible

alkyds⁹ produce highly adherent, hard and smooth films. These modified shellac varnishes have very satisfactorily been used in the preparation of anti-corrosive primers.

Lac-linseed oil-red oxide primer produces on baking at 150°C for 30 minutes hard, adherent and elastic films on ferrous metals. It also shows very good resistance to water, solvents, chemicals and corrosion. The most attractive features of this primer are that its film cuts clean in a machine without flaking or chipping and that it can be applied by the electro-painting technique.

The incorporation of corrosion inhibitors in order to improve still further the anti-corrosive properties of this primer has now been studied.

Corrosion inhibitors by virtue of their inhibitive action passivates the metal surface and thus check corrosion. It has been shown by J. L. Rosenfield¹¹, Meyer¹², Cole¹³ and Mayne¹⁴ that in the presence of corrosion inhibitors only a single coat of primer film becomes sufficient to protect the metal from corrosion because the protection of the surface is done by the inhibition of the anodic reaction of metal and not by the densification of the film.

In the present investigations, six well known corrosion inhibitors namely potassium chromate, sodium nitrite, n-butylamine, sodium benzoate, strontium chromate and sodium chromate have been evaluated.

Experimental

Preparation of the vehicle

The vehicle was prepared by blending aqueous solutions of shellac (60 parts) obtained by dissolving water soluble lac in warm water at 80°C and maleinised linseed oil (40 parts) both on dry basis. Maleinised oil for the above composition was prepared by reacting linseed oil (100 parts) with maleic acid (35 parts) at 210°C for two hours, washing the product thoroughly with water and dissolving the same in aqueous ammonia. A clear homogeneous varnish was obtained.

Preparation of primers

Primer compositions were prepared by grinding together the following ingredients in a ball mill for 18-20 hours — till thoroughly dispersed. The primers so obtained were strained through muslin to remove any coarse particle and other impurities.

Optimum proportion of the individual corrosion inhibitor was arrived at after making several preliminary trials by taking different quantities of corrosion inhibitors. One part of organic corrosion inhibitor and 10 parts of inorganic corrosion inhibitors per 1000 parts of the vehicle were found satisfactory.

COMPOSITION OF THE PRIMER

1	Water soluble lac — linseed oil vehicle (containing 60 parts lac and 40 parts maleinised linseed oil)	—	1000 parts
2	Red oxide of iron	—	180 "
3	Talc	—	10 "
4	Wet ground mica	—	18 "
5	Zinc oxide	—	5 "
6	Corrosion inhibitor	Organic —	1 "
		or	
		inorganic —	10 "

Preparation of test samples

Seven sets of mild steel panels (15 cms x 10 cms.) were cleaned free from rust, oily matter, dust etc. under the conditions recommended in ASTM-D 609-52 (standard method of preparation of steel panels). These panels were then dipped in 50 per cent phosphoric acid for 30 seconds, washed in running water and dried. The dried panels were then coated by all the three conventional methods viz. brushing, dipping and

spraying. Smooth and uniform finishes were obtained by all the methods. The coated panels after a flash off period of ten minutes were baked in an oven at 150°C for 30 minutes and the films were tested for mechanical and anti-corrosive properties after 24 hours of baking. Standard methods of testing as prescribed in ISS 101/1961 were followed.

Results and discussions

Mechanical properties

All the films obtained after baking at 150°C for 30 minutes were hard, adherent, and flexible. They showed good wetting and hold out to top coats such as synthetic enamels, oil paints, N.c. lacquers, etc. The results presented in table No. 1 show that the incorporation of corrosion inhibitors improve both mechanical as well as anti-corrosive properties. The primer containing sodium nitrite gave the best scratch resistance (< 2000 g) while the primer containing *n*-butylamine showed much improved flexibility, scratch hardness and impact resistance. As regards wet abrasion resistance all the panels behaved alike and stood the test satisfactorily.

Water resistant properties

Water resistance of primer films was determined by immersing the baked films in distilled water for 500 hours and noting the extent of blistering/blushing at regular intervals of time. The data given in table No. II show that the primers containing inorganic cor-

TABLE I
MECHANICAL PROPERTIES OF FILMS OF WATER THINNABLE LAC-MALEINISED LINSEED OIL-RED OXIDE PRIMER CONTAINING DIFFERENT INHIBITOR (FILMS BAKED AT 150°C — 30 MINUTES AND TESTED AFTER 24 HOURS OF BAKING)

Sl	Corrosion inhibitor used	*Scratch hardness "g"	†Impact resistance	@Flexibility	‡Abrasion resistance in the presence of pumice powder & water
1	None (control)	1300	Very fine cracks and No peeling	Micro cracks 1/8"	No damage
2	Potassium Chromate	1000	Peeled off	Cracks 1/8"	—do—
3	Sodium nitrite	<2000	Peeled off	Failed 1/2"	—do—
4	N-butylamine	1800	No crack and no peeling	No crack 1/8"	—do—
5	Sodium benzoate	1300	Fine cracks and no peeling	Cracks 1/4"	—do—
6	Strontium Chromate	1400	Fine cracks and no peeling	Cracks 1/2"	—do—
7	Sodium Chromate	1300	Peeled off	Failed 1/2"	—do—

N.B.

* Tested on electrically operated apparatus (sheens): Load on 1 mm. steel ball.

† Tested as per ASTM method (Falling block impact tester).

@ Tested on hand operated conical mandrel.

‡ Tested on electrically operated wet abrasion tester with pumice stone powder and water — 2000 rubs.

TABLE III
**PROPERTIES OF LAC-MALEINISED LINSEED OIL RED
 OXIDE PRIMER CONTAINING N-BUTYLAMINE**

1	Consistency	Smooth, Uniform, brushable and sprayable.
2	Time of flow in Ford Viscosity cup no. 4	20 secs.
3	Flash off period	7 to 10 minutes.
4	Baking temp. and time	150°C, 30 minutes.
5	Finish	Egg shell, flat.
6	Scratch hardness	1800 g.
7	Flexibility (conical mandrel)	Satisfactory.
8	Impact resistance	No damage.
9	Water resistance (500 hours)	No damage.
10	Corrosion resistance	
	(a) Humidity cabinet (1000 hours)	No damage to film and no corrosion spot on the metal.
	(b) Salt droplet test (100 hours)	
11	Coverage of the primer	22 sq. metres per litre with film thickness 1.5 mil.
12	Wt. per litre (solids 30 per cent)	1.25 kg.

rosion inhibitors invariably deteriorated the water resistance of the films. Maximum deterioration occurred with sodium nitrite. Organic inhibitors especially *n*-butylamine gave the best performance.

Anti-corrosive properties

Corrosion resistance of primer films was determined by three standard methods namely by humidity cabinet exposure, 1000 hours, salt drop-let test for 100 hours and sulphur dioxide exposure test for 100 hours. Both scratched (cross scratched) and unscratched panels were subjected to the above tests. The condition of the film as well as of the substrate was examined at regular intervals of time and it may be seen from table No. II that except *n*-butylamine all the corrosion inhibitors affected adversely the anti-corrosive properties of the primer.

Solvent and chemical resistant properties

Solvent and chemical resistant properties of the primer films were determined by immersing the panels in the respective solvent or chemical and also by hard rubbing the film on the panel by a cotton wool soaked in the respective solvent and noting the extent of damage caused to the film. The data presented in table No. 2 show that all the films behaved practically alike except that the primer film containing *n*-butylamine, which showed a little improved alkali resistance.

It was further noted that all the films after the above tests were intact. No sign of blistering or softening was noticed thus showing that these corrosion inhibitors do not affect the solvent and chemical resistance of the films to any appreciable extent.

Shelf life of primer compositions

Shelf life of primers containing different corrosion inhibitors was determined by noting the viscosity by No. 4 Ford cup at different intervals of time. The results show that primers containing potassium chromate, sodium nitrite, *n*-butylamine and sodium benzoate have a tendency to thin down with the lapse in time. In the first month this tendency is more but after wards it becomes substantially less. On the other hand primer containing strontium chromate and sodium chromate show thickening in the first instance and when diluted with water and stored they also show thinning tendency.

At the end of 18 months all the samples are keeping satisfactory. Though a little settling of pigment was noticed but after stirring it could be redispersed and a uniform primer could be obtained.

From the foregoing results it may be seen that out of the six corrosion inhibitors investigated only *n*-butylamine proved the most satisfactory and therefore this composition is recommended for use in industries particularly in automobile as baking type primer. The properties of this primer are presented in table No. III.

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TABLE II
 FILM CONDITION AND ANTI-CORROSIVE PERFORMANCE
 (Films baked at 150°C — 30 minutes. Tested under different conditions after 24 hours of baking after removal of primer film by conventional film)

Sl. no.	Corrosion inhibitor used	Water immersion — 500 hours —				Humidity cabinet exposure 100 hours			
		Scratched panel		Unscratched panel		Scratched panel		Unscratched panel	
		Film condition	Anti corros'ive performance	Film condition	Anti corros'ive performance	Film condition	Anti corros'ive performance	Film condition	Anti corros'ive performance
1.	Non (Control)	Very slight creepage	Very few creeping rust spot along scratch line	No blister	No rusting	Very slight creepage	Very few creeping rust spot along scratch	No blister	No rusting
2.	Potassium Chromate	Moderate creepage	Slight creeping rust along scratch line	A few small blisters	A few rust spots	Slight creepage	Creeping rust along scratch line	A few small blisters	Some rust spot
3.	Sodium nitrite	Considerable creepage	Considerable creeping rust along scratch line	Full of cracked blisters	Considerable rust spots	Moderate creepage	Considerable creeping rust	Full of small blisters	Considerable rusting
4.	n-butyl-amine	Unaffected	No creepage sharp scratch line	Unaffected	No rust spot	Unaffected	No creepage sharp scratch line	Unaffected	No rust spot
5.	Sodium benzoate	Little creepage	Little creepage along scratch line	Small uncracked blister	No rust spot	Little creepage	Creeping rust along scratch line	A few small blisters	No rust spot
6.	Strontium chromate	Slight creepage	Slight creeping rust along scratch line	Uncracked blisters	Very few rust spot	Slight creepage	Slight creeping rust along scratch line	A few small blisters	No rust spot
7.	Sodium chromate	Moderate creepage	Creeping rust along scratch line	Small cracked blisters	Some rust spots	Moderate creepage	Creeping rust along scratch line	Full of small blisters	Some rust spot

OF THE PRIMERS
) (Anti-corrosive performance: Metal surface condition
 remover)

Salt droplet exposure 100 hours					
Scratched panel		Unscratched panel		SO ₂ expo- sure 100 hours	Alkali resistance NaOH soln. 2 per cent Initial time of lifting minutes
Film condition	Anti corrosive performance	Film condition	Anti corrosive performance		
Very slight creepage	Little creeping rust along scratch line	Unaffected	No rusting	Few small blisters	10
Slight creepage along scratch line	Creeping rust along scratch line	Unaffected	No rusting	Blistered	10
Moderate creepage along scratch line	Moderate creeping rust along scratch line	Some blister spots	A few rusting spot	Few small blisters	15
No creepage	No rusting	Unaffected	No rusting	Very few blisters	25
Little creepage	No rusting	Unaffected	No rusting	Few small blisters	10
Slight creepage	No rusting	Unaffected	No rusting	Blistered	10
Moderate creepage	Creeping rust along scratch line	Few blister spots	Few rust spots	Moderately blistered	10