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Copper Based Antifouling Paints for Prevention of Marine Growth on Ship Hulls

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Abstract. The mode of action and requirements of ingredients of copper based antifouling paints used in the country for the prevention of fouling, on ship-hulls have been described. The studies on performance of antifouling paints based on cuprous oxide-chlorinated rubber-rosin system have also been reported.

Antifouling life improves with increase in concentration of cuprous oxide, 43 per cent by volume being the optimum toxic content. A minimum rosin to resin ratio of 3 : 1 is required to permit adequate release of copper for prolonged periods. Hydrolysable plasticizer namely tricresyl phosphate has been found to be superior to chlorinated paraffin wax for the design of antifouling compositions. The antifouling paint based on chlorinated rubber resin is expected to give a life of 15-18 months in service.

1. Introduction

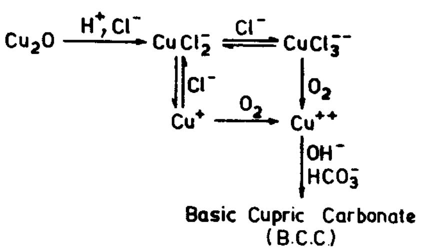
Antifouling paints have been most effective and also widely employed method for preventing of fouling of underwater portion of ships. These paints are applied over anticorrosive coatings to remain in contact with seawater. The antifouling paints contain toxic material(s) which are constantly released from the surface of the film into the seawater at a controlled rate inhibiting the growth of fouling organisms. Present day antifouling formulations utilise cuprous oxide as the main toxic agent. During the last 20 years, the efforts of NCML have led to the improvement in performance of antifouling paints to the extent that current coatings prevent fouling for periods of about 15-18 months even in Indian waters where fouling is more intense and occurs throughout the year[1]. This paper describes the mode of action and requirements of ingredients of copper based antifouling compositions. The studies on antifouling paints containing chlorinated rubber resin as one of the constituents of matrix have also been reported.

Mode of Action of Antifouling Paints

The toxic material from the coating must be released into the seawater at a rate high enough to maintain a poisonous environment at the paint film surface. The toxic layer at the interface retards the metabolic activity of animals' larvae and algal spores and inhibits their attachment at the surface. For copper, a minimum leaching rate of 10 μg/sq. cm/day, as determined in the laboratory at 20°C, is believed[1,3] to be necessary for prevention of fouling settlement.

An effective antifouling paint must maintain leaching rate at desired level for prolonged period. The paint is designed to provide for eventual dissolution of the cuprous oxide particles deeper into the film.

There are several ways by which the leaching of toxic cuprous oxide from the paint film is attained. One is by its diffusion of toxic into the seawater from the paint film leaving matrix skeleton behind. Such paints are known as insoluble matrix type and require high loading of cuprous oxide so that its particles are in contact with each other throughout the dried paint film. This continuous contact facilitates diffusion of copper from the depth of the film. Insoluble matrix antifouling paints require strong and tough synthetic resins like vinyls as matrices to ensure adequate physical integrity of the film. The release of toxic from the paint film of a continuous contact paint is controlled by the dissolution of cuprous oxide in seawater as indicated below:



Basic cupric carbonate formed by the reaction of cuprous oxide with seawater in the presence of oxygen is a mixture of basic cupric carbonate and cupric oxychloride. Its experimentally determined solubility has been found to be approximately 0.5 μg/ml. When this solubility product exceeds, a bluish green precipitate is formed and deposited on the paint surface. This gradually depresses leaching rate of copper from the coating. This is one of the factors, which comes in way in the design of very long life antifouling paints containing copper as toxic.

Another mechanism[1] for attaining steady state leaching of copper toxic is by simultaneous dissolution of the poison and vehicle. In this case there is a gradual consumption of the film and the composition could be effective till the paint film is completely exhausted. Such paints are described as soluble matrix type and contain much lower amounts of cuprous oxide than insoluble matrix paints. The leaching rate of these paints is dependant solely on the solution rate of vehicle.

Requirement of Biocidal Material

A material to function as an antifoulant must possess (a) wide spectrum biocidal activity to prevent settlement of majority of the organisms causing fouling of hulls, (b) lack of toxicity towards mammalians, and (c) requisite solubility in seawater to permit adequate release of the toxic for extended periods. The solubility of some copper compounds having well known biocidal activity is reproduced[1] in Table 1.

Table 1. Solubilities of copper compounds in seawater at pH 8.1

Compound	Solubility ($\mu g/ml$)	Source
Cupric citrate	>170,000	Exptl.
Cuprous chloride	31,000	Calcd.
Cuprous oxide	5.40	Exptl.
Basic cupric carbonate	0.50	Exptl.
Cupric hydroxide	0.013	Calcd.
Cupric oxide	0.001	Calcd.

Compounds like cupric oxide and hydroxide are not suitable for antifouling paints because their extremely low solubilitiy does not ensure adequate leaching of copper from the paint film. On the other hand compounds having high solubilities, such as cupric citrate and cupric chloride are lost quickly resulting in premature exhaustion of film. Moderately low solubility of cuprous oxide facilitates the desired leaching rate from a paint in which it is compounded. The leaching behaviour of the paint which determines the antifouling performance, also depends upon the proportion of the toxic in the formulation and the composition of the matrix.

Choice of the Matrix

The choice of the matrix is largely governed by the type of antifouling paints. Insoluble matrix type paints require strong and tough synthetic resins as their media to hold the pigments particles together. Vinyl resins are the most commonly used vehicle for such paints.

Rosin, a natural acidic resin, is the major constituent of the binder of soluble matrix type antifouling paints. Neutral materials like blown fish oil or synthetic resin like vinyl or chlorinated rubber as well as plasticizers are also added in appropriate proportions in the matrix. Rosin helps in the dissolution of the matrix and consequently cuprous oxide in seawater, by virtue of its being acidic in nature. Neutral material and plasticizers are needed to regulate the leaching rate of copper and provide improved mechanical strength to the paint film. Vinyl and chlorinated rubber resins are particularly suitable neutral materials, by virtue of their tough nature, for longer life antifouling paints containing relatively higher amount of cuprous oxide.

De *et al.*[5] have reported studies on performance of antifouling paints based on cuprous oxide-vinyl resin-rosin system. The present paper covers studies on antifouling paints based on cuprous oxide-chlorinated rubber resin-rosin system.

2. Experimental

The antifouling paints were formulated using indigenous chlorinated rubber resin (Chlorub-20). The requisite amount of chlorinated paraffin wax was incorporated as plasticizer. Zinc oxide was used as stabilizer.

Antifouling compositions (CRAF 1–24) containing cuprous oxide between 30 and 48 per cent by volume and having varying rosin to resin ratio (1 : 2 to 5 : 1 by volume) in the binder were prepared. Compositions totally free from rosin were also prepared and assessed for the purpose. In addition, fifteen antifouling paints (CRAF 25–39), incorporating three plasticizers namely tricresyl phosphate, dioctyl phthalate, dibutyl phthalate and also a mixture of equal parts of chlorinated paraffin wax and tricresyl phosphate, were compounded. Salient features of antifouling compositions examined are given in Tables 2 & 3.

Table 2. Salient features of chlorinated rubber based antifouling paints (Rosin-Resin-Cuprous Oxide)

Composition	Cuprous oxide (%)	Rosin : Resin	Total soluble (%)
CRAF 1	30	1 : 2	44.4
CRAF 2	30	1 : 1	50.1
CRAF 3	30	2 : 1	56.8
CRAF 4	30	3 : 1	60.2
CRAF 5	30	5 : 1	63.5
CRAF 6	30	No rosin	30.0
CRAF 7	36	1 : 2	48.2
CRAF 8	36	1 : 1	54.3
CRAF 9	36	2 : 1	60.4
CRAF 10	36	3 : 1	63.5
CRAF 11	36	5 : 1	66.5
CRAF 12	36	No rosin	36.0
CRAF 13	43	1 : 2	53.8
CRAF 14	43	1 : 1	59.2
CRAF 15	43	2 : 1	64.6
CRAF 16	43	3 : 1	67.3
CRAF 17	43	5 : 1	70.0
CRAF 18	43	No rosin	43.0
CRAF 19	48	1 : 2	57.8
CRAF 20	48	1 : 1	62.7
CRAF 21	48	2 : 1	67.6
CRAF 22	48	3 : 1	70.5
CRAF 23	48	5 : 1	72.5
CRAF 24	48	No rosin	48.0

Raw Materials

Resins—Chlorinated rubber used is a white amorphous powder containing about 65 per cent chlorine and having a viscosity range of 18–24 centipoises (measured using 20 per cent w/w resin solution in toluene by Ostwalds viscometer at 25°C). It has a specific gravity of 1.36. Gum Rosin (w w grade), an acidic natural resin used had an acid value of 160 mg of KOH per gram of resin and conformed to IS : 553–1969.

Plasticizers—Chlorinated paraffin wax has chlorine content of 40 $\pm$ 1% (by weight) when determined by ASTM D 1303–55 using Parr Peroxide Bomb and a

Table 3. Salient features of chlorinated rubber based antifouling paints (Rosin —Resin—Plasticizers)

Composition	Rosin : Resin	Plasticizer	Total soluble (%)
CRAF 25	2 : 1	CP+TCP	75.4
CRAF 26	3 : 1	CP+TCP	78.1
CRAF 27	5 : 1	CP+TCP	80.8
CRAF 28	2 : 1	TCP	86.2
CRAF 29	3 : 1	TCP	88.9
CRAF 30	5 : 1	TCP	91.6
CRAF 31	No rosin	TCP	64.6
CRAF 32	2 : 1	DBP	86.2
CRAF 33	3 : 1	DBP	88.9
CRAF 34	5 : 1	DBP	91.6
CRAF 35	No rosin	DBP	64.6
CRAF 36	2 : 1	DOP	86.2
CRAF 37	3 : 1	DOP	88.9
CRAF 38	5 : 1	DOP	91.6
CRAF 39	No rosin	DOP	64.6

molecular weight of 550 $\pm$ 20. Plasticizers namely tricresyl phosphate (TCP), dibutyl phthalate (DBP) and dioctyl phthalate (DOP) conformed to ASTM specifications D 363–56 (1975), D 608–58 (1970) and D 1249–69 (1976) Type I, respectively.

Pigments and Extenders—Cuprous oxide pigment was of electrolytic grade and conformed to the specification IS : 70 – 1950. It contained 94 per cent cuprous oxide. Zinc oxide conformed to standard IS : 35 – 1950.

Solvents—Commercial grades of Xylene, White spirit and Solvent C IX (consisting mainly of trimethylbenzenes with aromaticity of 90 per cent) were used for the formulation of paints.

Method of Preparation of Experimental Paints

The required amount of chlorinated rubber resin, plasticizer, cuprous oxide and zinc oxide, premixed with adequate amount of solvent, were ground in the laboratory sand mill to a fineness of grind of 3–5 on the Hegman scale. The mill base was taken out and mixed with the rosin solution prepared separately in xylene. Paint of brushing consistency was obtained by adding further quantities of solvent mixture.

Evaluation of Antifouling Paints

The paints were evaluated for their antifouling property by exposing them on the experimental raft moored in Bombay harbour. Perspex panels (250 $\times$ 150 $\times$ 6 mm) were selected for the exposure to eliminate interference from corrosion. The panels were abraded with emery paper (1G) and a coat of wash primer conforming to specification DTD 868 was applied to ensure satisfactory adhesion of the paint film on the substrate. The compositions were applied in two coats by brushing to give a total dry film weight of 13.5–24.0 gm (180–320 gm/m^2).

The panels were rigidly fixed to the exposure frames and immersed in the sea from raft after 24 hours of drying of final coat of the paint. Each composition was immersed in duplicate at depths of 60 and 120 cm.

Method of Assessment

Inspection of panels was carried out at monthly intervals. Assessment was carried out by direct rating method described in literature[1]. Performance has been expressed as fouling resistance which is 100 per cent minus the percentage area which has permitted attachment. A penalty of five per cent has been deducted from the ratings for slime, scum and incipient fouling.

Accelerated Leaching Rate Characteristics

Leaching rate characteristics of selected paints were determined by accelerated leaching rate method[6]. A coat of paint was applied on perspex test panels. Panels were subjected to mechanical agitation in alkaline glycine solution (pH 10.5). At the end of every eight hour period, leachates were removed. The copper content in the leachate was determined by colorimetric method using spekker absorptiometer. The leaching rate-time curves were derived for the compositions.

Examination of Mechanical Properties

Mechanical properties of a few paints containing different plasticizers were examined using bend test (cylindrical mandrel) and universal cupping test equipments.

3. Results and Discussion

Leaching characteristics and consequently antifouling property of a given formulation depends upon the concentration of cuprous oxide and ratio of rosin to inert resin, the latter being incorporated to regulate the release of biocide. Nature of plasticizer also affects the protective efficiency of antifouling paints[7-9]. Two series of compositions were prepared in order to examine the effect of ingredients on the performance of chlorinated rubber antifouling compositions.

The compositions under series I (Table 2) were examined to ascertain the effect of cuprous oxide loading and level of rosin in the binder. The relative efficiency of various plasticizers was judged by the formulations included in series II (Table 3). In this series cuprous oxide concentration was kept constant (43 per cent by volume).

Experimental antifouling compositions were evaluated by exposing in the raft moored in Bombay harbour (latitude 18°55′). Performance of the experimental paints has been expressed in terms of per cent fouling resistance. Paint is considered satisfactory so long as fouling resistance rates 95 per cent. Rating below 80 per cent is considered unsatisfactory. Ratings between 95 and 80 are considered to indicate good or fair performance. Detailed results of 24 months exposure are given in Tables 4 & 5. It can be seen from these tables that antifouling life of paints varies from less than 6 months to 24 months. The antifouling property improves with increase in loading of cuprous oxide as well as levels of rosin.

Table 4. Performance of chlorinated rubber based antifouling paints
(Rosin-Resin-Cuprous Oxide)

Composition	Per cent fouling resistance after			
	6 months	12 months	18 months	24 months
CRAF 1	35	0	0	0
CRAF 2	65	0	0	0
CRAF 3	95	95	35	0
CRAF 4	95	95	65	30
CRAF 5	95	95	75	50
CRAF 6	0	0	0	0
CRAF 7	30	0	0	0
CRAF 8	85	55	0	0
CRAF 9	95	95	50	20
CRAF 10	95	95	80	60
CRAF 11	95	95	95	65
CRAF 12	45	0	0	0
CRAF 13	95	60	0	0
CRAF 14	95	75	50	35
CRAF 15	95	95	70	45
CRAF 16	95	95	95	70
CRAF 17	95	95	95	70
CRAF 18	85	0	0	0
CRAF 19	95	70	0	0
CRAF 20	95	85	40	0
CRAF 21	95	95	90	75
CRAF 22	95	95	95	90
CRAF 23	95	95	95	95
CRAF 24	95	70	0	0

Table 5. Performance of chlorinated rubber based antifouling paints
(Rosin-Resin-Plasticizers)

Composition	Per cent fouling resistance after			
	6 months	12 months	18 months	24 months
CRAF 25	95	95	95	70
CRAF 26	95	95	95	85
CRAF 27	95	95	95	95
CRAF 28	95	95	95	90
CRAF 29	95	95	95	90
CRAF 30	95	95	95	95
CRAF 31	95	95	80	65
CRAF 32	95	95	90	20
CRAF 33	95	95	85*	0
CRAF 34	95	95	75*	0
CRAF 35	95	95	65	0
CRAF 36	95	95	90	75
CRAF 37	95	95	90	85
CRAF 38	95	95	90	85
CRAF 39	95	95	65	45

*Film shows erosion

The leaching rate values of antifouling paints have also been determined by accelerated glycine method and are illustrated in Figs. 1–5. The accelerated leaching rate technique has been employed as a qualitative method for comparison of leaching behaviours of similar antifouling formulations.

Effect of Cuprous Oxide

Study conducted by De *et al.*[5] indicates that long life antifouling compositions could be formulated with cuprous oxide between 30 and 50 per cent by volume. Concentrations of cuprous oxide between 30 and 48 per cent by volume have, therefore, been examined in the present study. It can be seen from Fig. 1 that compositions plasticized with chlorinated paraffin wax do not show adequate leaching characteristics even with cuprous oxide concentration as high as 48 per cent by volume. Consequently compositions show poor antifouling property in raft trials (Table 4). These compositions belong to the class of insoluble matrix paints where continuous contact of pigment particles in the film is required to obtain adequate leaching from the paint coating. Theoretically, this contact between particles is achieved at pigment concentrations from 52 to 74 per cent by volume exhibiting varying packing patterns. A concentration of 52 per cent will provide a cubic packing pattern while 74 per cent will result into a hexagonal packing pattern. Composition CRAF 24 plasticized with chlorinated paraffin wax and containing 51 per cent pigment volume concentration has not shown adequate leaching properties although cubic packing of pigment particles is expected in the formulation.

The leaching characteristics and antifouling property improve with increase in pigment volume concentration if rosin is present in the binder plasticized with

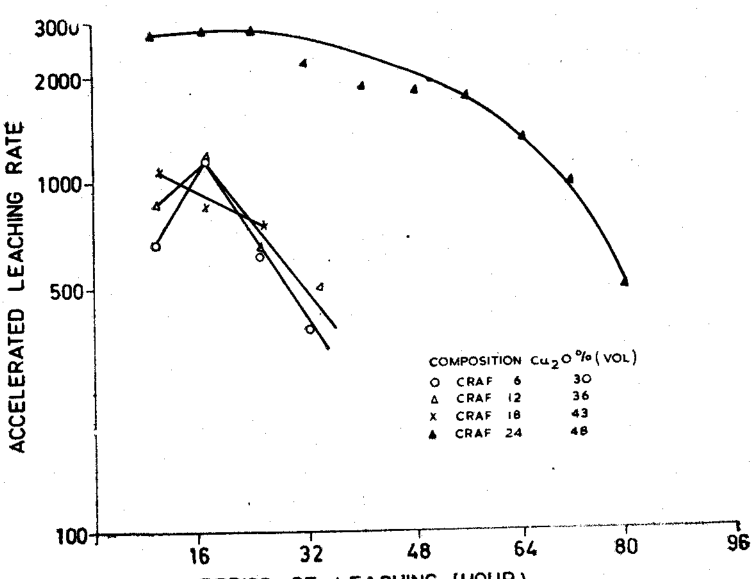


Figure 1. Leaching behaviour of rosin free antifouling paints containing different amount of cuprous oxide and Chlorinated paraffin wax. (Accelerated leaching rate μg of $Cu/cm^2/day$)

chlorinated paraffin wax (Fig. 2, Table 4). A significant improvement in antifouling property even at 43 per cent cuprous oxide concentration has also been observed when chlorinated paraffin wax is replaced by saponifiable plasticizers namely tricresyl phosphate and dioctyl and dibutyl phthalates. This could be explained on the basis of concept put forth by Van London[10] that cuprous oxide, rosin and/or saponifiable plasticizers constitute the total solubles of the paint. Increase in total solubles by incorporation of any of the three ingredients assists in achieving the continuous contact of pigment particles and at the same time promotes diffusion of copper from paint film leading to longer steady state leaching rates. Results of this study have confirmed the observation of Van London that the total solubles amounting to more than 60 per cent of the composition is necessary to ensure adequate release of the poison from the film. Increase in total solubles facilitates availability of copper from the film.

Effect of Rosin

Rosin in the binder plays an important role in the release of copper from the film. Increase of rosin in the matrix improves leaching properties of the formulations (Fig. 3). It has been observed that a minimum rosin to resin ratio of 2 : 1 is required for adequate leaching of copper for periods extending to over nine months. Better results still are obtained at a ratio of 3 : 1 (Fig 3, Table 4). This amount of rosin provides desired solubility to the binder permitting simultaneous dissolution of vehicle and toxic. The gradual consumption of the film ensures prolonged steady state leaching rates to the formulations.

Relative Efficiency of Plasticizers

Plasticizers are added to paint formulations to improve mechanical properties of the films. In the case of antifouling paints, they may, depending upon their hydrolysability, play an additional role of regulating the leaching of copper from the film. The antifouling and mechanical properties of compositions containing chlorinated paraffin wax, TCP, DOP and DBP were evaluated in order to ascertain the relative merit of these plasticizers. Formulations containing both these plasticizers and the other ingredients at fixed concentrations were considered for this evaluation. Results are given in Table 6 & 7.

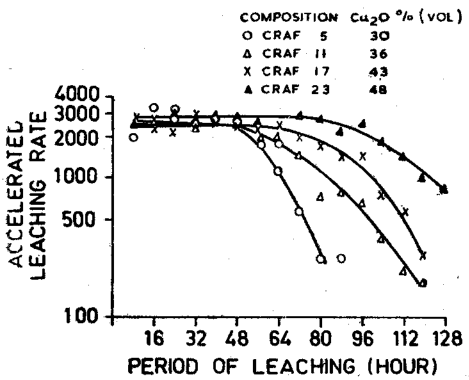


Figure 2. Leaching rate characteristics of antifouling paints with rosin to resin ratio of 5 : 1 and different PVC of cuprous oxide. (Accelerated leaching rate μg of Cu/cm^2/day)

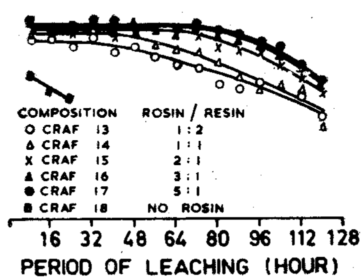


Figure 3. Leaching rate characteristics of antifouling paints with cuprous oxide PVC of 43% and different rosin to resin ratio. (Accelerated leaching rate μg of Cu/cm^2/day)

Table 6. Performance of chlorinated rubber based antifouling paints with different plasticizers (cuprous oxide 43% by vol.)

Composition	Rosin : Resin	Plasticizer	Per cent fouling resistance after		
			12 months	18 months	24 months
CRAF 16	3 : 1	CP	95	95	70
CRAF 29	3 : 1	TCP	95	95	90
CRAF 33	3 : 1	DBP	95	85*	0
CRAF 37	3 : 1	DOP	95	90	85
CRAF 17	5 : 1	CP	95	95	75
CRAF 30	5 : 1	TCP	95	95	95
CRAF 34	5 : 1	DBP	95	75*	0
CRAF 38	5 : 1	DOP	95	90	85
CRAF 18	No Rosin	CP	0	0	0
CRAF 31	No Rosin	TCP	95	85	35
CRAF 35	No Rosin	DBP	95	65	25

* Film shows erosion

Table 7. Mechanical properties of antifouling composition containing different plasticisers

Composition	Rosin : Resin	Plasticizer	Film thickness	Bend test	Cupping value (mm)
CRAF 17	5 : 1	CP—40	2.5	Poor	1.25
CRAF 27	5 : 1	CP—40+TCP (1 : 1)	2.5	Good	6.0
CRAF 30	5 : 1	TCP	2.75	Good	7.6
CRAF 34	5 : 1	DBP	2.5	Poor	1.65
CRAF 38	5 : 1	DOP	2.25	Poor	1.6

It can be seen from the Table 6 that amongst the four plasticizers, chlorinated paraffin wax does not assist in providing adequate antifouling efficiency to the composition. The leaching behaviour (Fig. 4) of such composition is also poor.

Ester type hydrolysable plasticizers, TCP, DOP and DBP have undoubtedly shown superior performance to that of non-hydrolysable chlorinated paraffin wax. Antifouling compositions containing these plasticizers can be rated to possess fouling resistance of 95 per cent for 12 months (Table 6). These plasticizers are capable of undergoing hydrolysis by seawater, promoting diffusion of copper from the paint film. As judged by raft exposure trials, the efficacy of TCP, DOP and DBP incorporated in the compositions has been found to decrease in that order (Table 6) This performance has also been observed in leaching rate studies (Fig. 4). However, the steady state leaching rates of the compositions are not in conformity with the raft life. This variation in the behaviour could be due to excessive solvent property of the leaching solution. The leaching solution being alkaline may preferentially attack the plasticizer

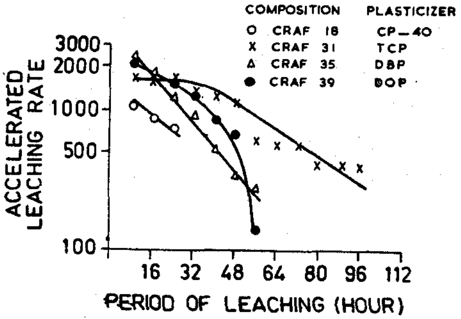


Figure 4. Leaching behaviour of rosin free antifouling paints containing different plasticizers. (Accelerated leaching rate μg of Cu/cm^2/day)

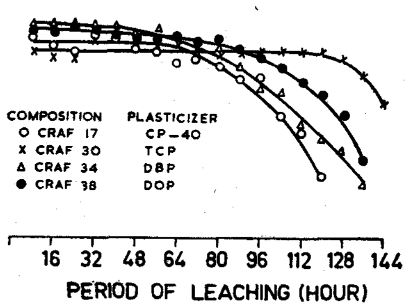


Figure 5. Leaching rate characteristics of antifouling paints containing different plasticizers in presence of rosin. (Accelerated leaching rate μg of Cu/cm^2/day)

extracting them at disproportionate rate. In seawater conditions (pH 8.2), reaction proceeds slowly giving extended antifouling performance.

In compositions containing rosin, effect of plasticizers has been observed to be less pronounced since the former plays a dominant role in controlling the release of copper. Behaviour of plasticizers in such compositions is shown in Fig. 5 and Table 6. It can be seen from the results that even chlorinated paraffin wax has given good results in formulations having rosin. Tricresyl phosphate has shown the most satisfactory performance amongst all the plasticizers examined. Composition containing this plasticizer (CRAF 30) has shown 95 per cent fouling resistance for 24 months. Antifouling paint film containing dibutyl phthalate (CRAF 33 & 34) is susceptible to wear due to excessive dissolution. This could be related to its higher rate of hydrolysis as compared to other saponifiable plasticizers. Further, DBP owing to its lower molecular weight would provide films having higher moisture permeabilities[11] and may aid faster dissolution of the film.

In respect of plasticizing efficiency, TCP alone provides good elasticity to the film (Table 7). Even replacement of 50 per cent of chlorinated paraffin wax with TCP results into improved film properties. The other three plasticizers fail to give adequate mechanical properties to the paint film.

4. Conclusion

Antifouling life improves with increase in concentration of cuprous oxide with 43 per cent by volume as optimum toxic content. A minimum rosin to resin ratio of 3 : 1 is required to permit adequate release of copper from formulation of satisfactory antifouling paint.

Hydrolysable plasticizer namely tricresyl phosphate has been found to be superior to chlorinated paraffin wax for formulating antifouling compositions.

The antifouling paint based on chlorinated rubber resin is expected to give a service life between 15–18 months.

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