HIGH BUILD ANTIFOULING PAINTS BASED ON DISPROPORTIONATED CALCIUM RESINATE

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ABSTRACT

Disproportionated calcium resinate was manufactured from disproportionated WW rosin and its fundamental characteristics were determined in laboratory tests.

Some experimental binders were formulated with disproportionated calcium resinate as soluble film forming material and also with WW rosin, disproportionated WW rosin and calcium resinate which were used as reference.

Then high build soluble antifouling paints based on the above mentioned binders with red cuprous oxide as the main toxicant were manufactured and tested in raft trials for 33 months: a series of painted panels was exposed to air for 24 hours and another one for 30 days previous to seawater immersion.

Some antifouling paints based on disproportionated calcium resinate displayed good bioactivity at the end of the test, their behaviour being unaffected by the exposure to air previous testing.

KEYWORDS:

antifouling paint, binder, cobinder, soluble matrix, high build, dissolution rate, bioactivity, raft trial.

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INTRODUCTION

New products and raw materials applied to the manufacture of antifouling paints are constantly being researched and developed. One of the advantages of this fact, from a chemical and a biological point of view, is that it obliges formulations to be modified with the aim of attaining higher efficiency and simultaneously decreasing pollution of the marine environment.

In this paper, a disproportionated calcium resinate was prepared with the aim of studying the influence of different variables of composition of antifouling paints based on this resinous material, using samples formulated with WW rosin /1/, disproportionated WW rosin /2/ and calcium resinate /3/ as references.

FORMULATION OF DISPROPORTIONATED CALCIUM RESINATE

Starting from WW rosin as raw material, a disproportionated WW rosin was firstly formulated by adding iodine at 260 °C and then furfural at 70 °C, according to a method described in a previous paper /2/.

Employing finely divided disproportionated WW rosin, a disproportionated calcium resinate was prepared adding an aqueous solution of sodium hydroxide, heating at 80°C up to its complete solubilization. In the same conditions a solution of calcium chloride was added, forming after five minutes of intense stirring a yellow, homogeneous and consistent paste. It was repeatedly washed with distilled water in order to eliminate the sodium chloride formed.

After approximately 10 hours at 45 °C a white powder of small diameter particles of disproportionated calcium resinate was obtained.

FORMULATION VARIABLES

The composition of paints is shown in Table I. Several variables were considered:

Type of soluble resinous materials

WW rosin, disproportionated WW rosin, calcium resinate and disproportionated calcium resinate were selected as film formers.

Table I
Composition of the antifouling paints (solids by volume, %)

Composition	A	B	C	D
Cuprous oxide	10.0	10.0	12.7	12.7
Zinc oxide	1.0	1.0	1.3	1.3
Calcium carbonate	28.4	28.4	25.4	25.4
Soluble resin*	24.4	34.0	24.4	34.0
Cobinder	24.4	17.0	24.4	17.0
Plasticizer	7.0	4.8	7.0	4.8
Additives	4.8	4.8	4.8	4.8
Soluble resin/cobinder ratio by volume	1/1	2/1	1/1	2/1

* Each one of the experimental samples was prepared by employing WW rosin, disproportionated WW rosin, calcium resinate or disproportionated calcium resinate

With the object of evaluating the characteristics of the resinous materials, fusion point (capillary method), melting point (ball and ring method, ASTM E 28-92) and acid number (inside indicator method, ASTM D 465-92) were determined.

The color of transparent solutions based on above mentioned resins and an adequate solvent through comparison with Gardner standards, according to ASTM D 1544-80, and density of the samples at 20 °C, were also determined.

Infrared spectra of the resins were carried out by applying the method of the solid phase: each material was dissolved in toluene and then was extended on a mounting which is transparent to the infrared radiation (potassium bromide). After the solvent was evaporated in vacuum, film was lifted off the substrate and fixed in the frame to place it in the path of the rays.

Soluble resinous material/cobinder ratio.

In order to study the influence of this variable on the dissolution rate of the different paints, two resinous material/cobinder ratios were established (1/1 and 2/1 by volume) giving the second one a binder of higher dissolution rate.

The cobinder employed was a non-modified copolymer of medium molecular weight, consisting of 86% vinyl chloride-14% vinyl acetate, which offers an adequate balance of the following characteristics: it shows an easy dissolution in cellosolve acetate/xylene/methyl isobutyl ketone mixture (60/30/10 ratio by weight) /4/ and also leads to films with good physical properties.

42 per cent chlorinated paraffin was used as plasticizer since it improves binder flexibility and reduces solvent retention.

Employing a high rate impeller, 8 binders (4 soluble resins x 2 soluble resin/cobinder ratios) were formulated.

Toxicant content.

Cuprous oxide was selected as fundamental toxicant /5-8/, zinc oxide as reinforcing pigment (10 % by volume respect to the mentioned toxicant) and calcium carbonate (chalk) as extender.

Two levels of cuprous oxide were considered: 10.0 % and 12.7 %, expressed as solids by volume on paint. With the aim of disposing of high pigment contents but without seriously affecting the film characteristics, only one volume pigment concentration (PVC 39.4 %) was selected in all the cases.

FORMULATION OF EXPERIMENTAL PAINTS

Samples were manufactured by employing a ball mill of 3.3 liters capacity /9,10/. The four series of paints based on WW rosin, disproportionated WW rosin, calcium resinate and disproportionated calcium resinate were prepared by first dispersing the zinc oxide and the calcium carbonate and then the cuprous oxide. After the last one was added, the process went on for 3 hours.

Finally the rheological additive was incorporated to each sample by employing the afore-mentioned high rate impeller: a gel of amorphous silicic acid with 5% by weight was used, selecting a level of 2.0% by weight on the total paint in order to achieve good rheological properties and easy airless spray application.

A similar set of paints was prepared but using only 1.0 % of thixotropic additive in order to have conventional products which were colored with blue, red or yellow pigments so as to facilitate the visual observation to estimate film thickness decreasing on service.

RAFT TESTING VARIABLES

The performance of the antifouling paints was evaluated on the experimental raft anchored at Puerto Belgrano (38°54'S; 62°06'W), area whose hydrological and biological conditions were studied /11,12/.

Steel panels, SAE 1010, were sandblasted to the grade ASa 2 1/2, washed with xylene and covered with an anticorrosive coating (two coats, 120-150 μm of dry film thickness) and a sealer (one coat, 50-60 μm). This scheme had been proved successful in previous trials.

After 24 hours, the experimental antifouling samples were applied. Panels were covered with three coats of the formulated thixotropic products (approximately 300 μm of total dry film thickness). Other series of panels with 6 coats of conventional colored products were prepared, also reaching about 300 μm of total dry film thickness.

In all cases the time between coats was 24 hours, the panel edges being retouched by brush. A series of panels was exposed to air for 24 hours and a similar one for 30 days for weathering previous to seawater immersion.

RESULTS AND DISCUSSION

Characteristics of the soluble resinous material

Table II shows the values of fusion and melting points for WW rosin and disproportionated WW rosin measured in the laboratory; both materials have perfectly defined values which allow the characterization of the resins. However these methods could not be applied to both calcium resinates since at low temperatures they did not display any modification and besides when they were heated over 200°C they showed clear signs of decomposition.

Acid number determination was also very useful; this value decreased from 160 to 139 through the disproportionating process of the original rosin giving a mixture of dehydro, dihydro and tetrahydroabietic acids. The acid value of the disproportionated calcium resinate was as expected (lower in relation to the natural WW rosin and disproportionated WW rosin).

Color comparison of the resins solutions according to ASTM D 1544-80 also was a method of easy application; it showed a color decreasing according to the transformation of the original resin (disproportion in a first stage and after this partial neutralization).

Table II

Characterization of the resinous materials

Test	WW rosin	Disproportionated WW rosin	Calcium resinate	Disproportionated calcium resinate
Fusion point, °C	75	68	--	--
Melting point, °C	57	50	--	--
Acid number	160	139	29	25
Color Gardner	7	4	3	2
Density (20°C), g/ml	1.08	1.11	1.13	1.18

Infrared spectra of both calcium resinates (Fig. 1 and 2) display in the zone of wave number 3400-3250 cm^{-1}, the overtone of the present peaks at 1720 cm^{-1} corresponding to the carbonyl group of esters. In the zone of wave number 3200-2800 cm^{-1} both calcium resinates show a significant thinning of the resinates peak with respect to both rosins, according to an important decreasing of the acid dimers. This is also confirmed by the disappearance of the peaks in the zone 1300-1100 cm^{-1} of the disproportionated WW rosin spectrum which is also attributable to the stretching of the C-O bond at 1475 cm^{-1} and 1180 cm^{-1} in the carboxyl group of the acids. Finally at 1560-1540 cm^{-1} a peak appeared that corresponds to the stretching of the acid group characteristic of salts.

Immersion trial. Bioactivity

Raft trials were programmed in order to observe periodically the painted panels and to record the fouling settlement after 4, 16, 28, and 33 months of immersion; the last one includes three periods of intense biological activity of the fouling organisms (spring-summer).

Sandblasted non-toxic acrylic panels submerged at the same depth as the ones mentioned were employed as reference of fouling fixation.

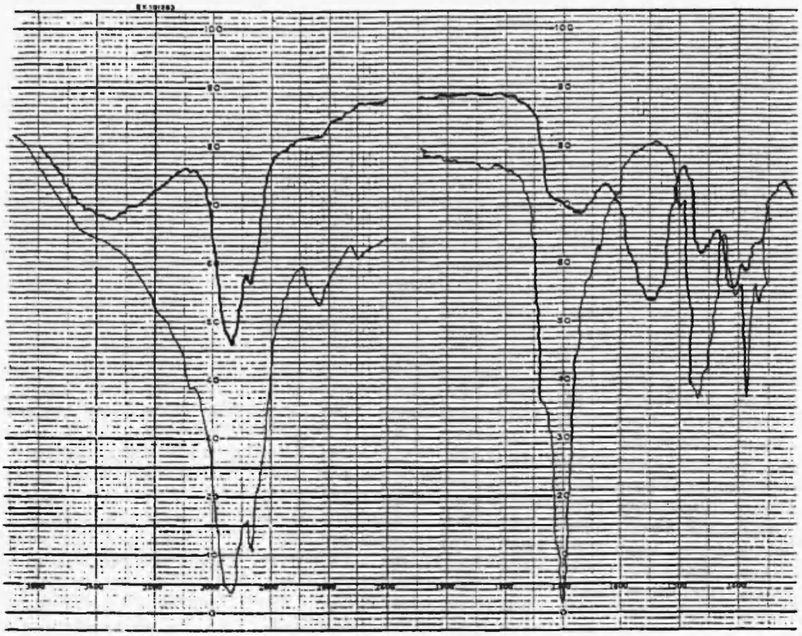


Fig. 1: Infrared spectra of the WW rosin resin (fine stroke) and calcium resinate (thick stroke).

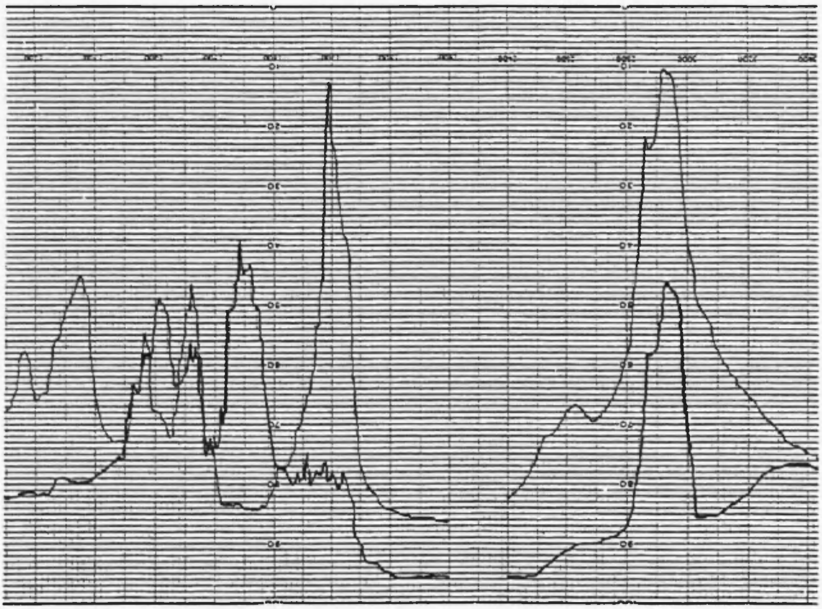


Fig. 2: Infrared spectra of disproportionated WW rosin (fine and disproportionated calcium resinate (thick stroke).

Fouling settlement evaluation, which allows the performance or bioactivity degree of each sample to be judged, was done by applying the scale mentioned in previous papers /13,14/. Value 0 (100 % of efficiency) corresponds to a panel without settlement and 5 (0 % of efficiency) to the one totally fouled; value 1, which corresponds to 80 % of efficiency, was fixed as the maximum limit for acceptance of a paint from the antifouling point of view.

In all cases the observations were complemented by means of color prints which allowed the results obtained in the different observations to be compared and to have a homogeneous evaluating criterion.

The conclusions of the inspections are included in Tables III and IV (24 hours and 30 days of exposure to air previous testing respectively). To a minimum biocidal efficiency of 80% (settlement 1, little), the useful life of each paint and also the film thickness required to achieve the before mentioned behaviour are pointed out.

A great influence of the several variables considered (soluble resinous material type, soluble resinous material/cobinder ratio, toxicant content and exposure time to air after painting and before seawater immersion) was observed. The analysis of results from experiments carried out in the present study and some conclusions previously drawn allows the advantages and disadvantages of the various resinous materials studied to be set out.

Table III

Biocide behaviour of the paints

24 hours of air exposure before immersion

Formulation	Soluble resin	Efficient time, months	Fixation grade, %	Required film thickness (minimum), μm
A	Original WW rosin	16	80	150
B		28	80	250
C		16	90	150
D		33	100	250
A	Disproportinated WW rosin	16	80	150
B		28	90	250
C		16	90	150
D		33	90	250
A	Calcium resinate	16	80	100
B		28	90	200
C		16	80	100
D		33	90	200
A	Disproportionated calcium resinate	16	80	100
B		28	90	200
C		16	90	100
D		33	100	200

Table IV

Biocide behaviour of the paints

30 days of air exposure before immersion

Formulation	Soluble resin	Efficient time, months	Fixation grade, %	Required film thickness (minimum), μm
A	Original WW rosin	28	80	250
B		33	100	>300
C		33	100	250
D		33	100	>300
A	Disproportinated WW rosin	16	80	150
B		28	80	250
C		16	90	150
D		33	100	250
A	Calcium resinate	16	80	150
B		28	100	250
C		28	90	200
D		33	100	300
A	Disproportionated calcium resinate	16	80	100
B		28	90	200
C		16	80	100
D		33	100	200

CONCLUSIONS

Original WW rosin

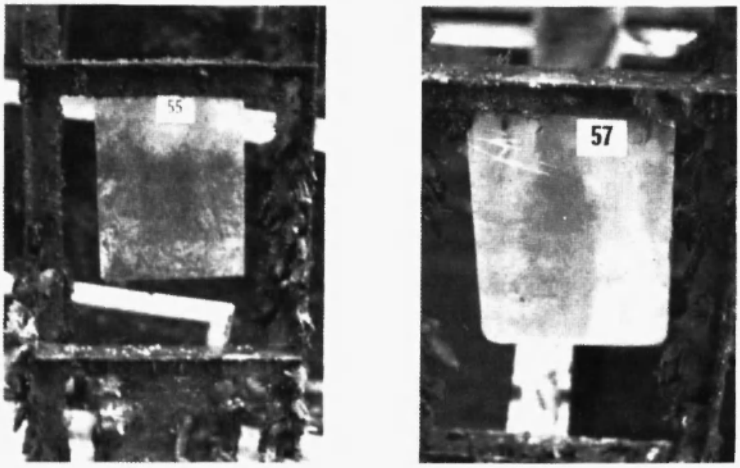
Advantages. Due to its physical and chemical properties, rosin is a natural resin widely used in the paint industry. It consists of nearly 85 per cent of resinous acids (abietic acid and its isomers) and the rest are complex esters of those acids with unsaponifiable materials. Due to its acid nature, rosin is the main binder component in soluble antifouling paints since it regulates the leaching rate of the toxic pigments. Toxicant content can range between extensive limits if binder dissolution rate is selected to have in film/seawater interface the adequate toxicant concentration to prevent fouling settlement. Efficient antifouling paints have been developed worldwide for long immersion times using WW rosin. Paints based on binders with the 2/1 WW rosin/cobinder ratio showed a higher seawater dissolution rate (less remainder dry film thickness) as well as a longer useful life than the paints formulated with 1/1 ratio binders. Fig. 3.1 displays the excellent behaviour (100 % of efficiency) corresponding to the paint D (original WW rosin, 24 hours of air exposure before seawater immersion) for 33 months on raft.

Disadvantages. The molecule of abietic acid has a carboxyl group which is responsible during immersion for the reaction with sodium and potassium ions to give a rapid initial dry film decrease and a high undesirable toxicant release; the reaction with calcium and magnesium ions reduces the dissolution rate. The previously mentioned reaction with divalent cations also takes place during paint manufacture, particularly when cuprous oxide and calcium carbonate are employed in the formulations. Cuprous oxide generates cupric oxide and metallic cooper [15] forming cupric resinates, which diminishes the binder dissolution rate and therefore the toxicant leaching rate [8, 9]. The pigment-binder reaction, which significantly depends on cuprous oxide dispersion time, modifies the composition of the paint and reduces the film bioactivity. However, when the afore-mentioned toxicant dispersion takes place in the absence of WW rosin, or when it is adequately controlled, paint bioactivity remains practically unmodified.

Another important disadvantage is the fact that when paint films based on WW rosin are exposed to air previous to seawater immersion, oxidation takes place and as a consequence, binder dissolution rate increases according to the exposure time and then a higher dry film thickness is required. This is not convenient from a technical, economical and ecological viewpoint since a higher toxicant leaching rate than the critical value takes place. Fig. 4.1 shows the very good biocidal capacity (100 % of efficiency) of sample D

3.1. WW rosin resin
Dry film thickness
required, minimum 250 μm
Efficiency, 100 %

3.2. Disproportionated WW rosin
Dry film thickness
required, minimum 250 μm
Efficiency, 90 %

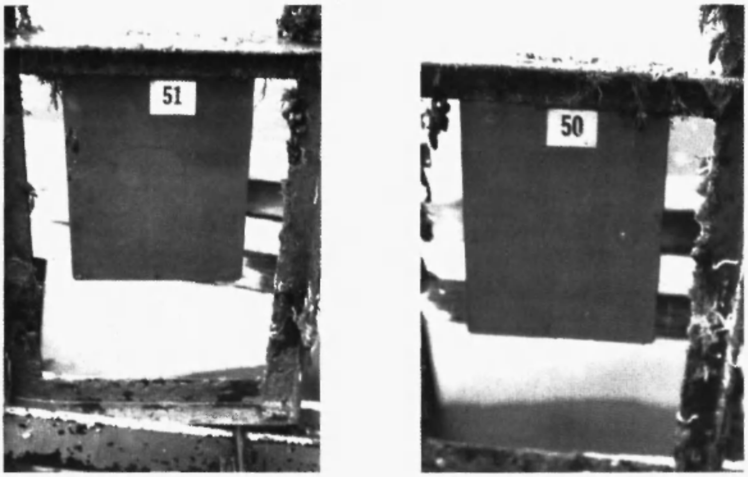


3.3. Calcium resinate
Dry film thickness
required, minimum 200 μm
Efficiency, 90 %

3.4. Disproportionated calcium resinate
Dry film thickness
required, minimum 200 μm
Efficiency, 100 %

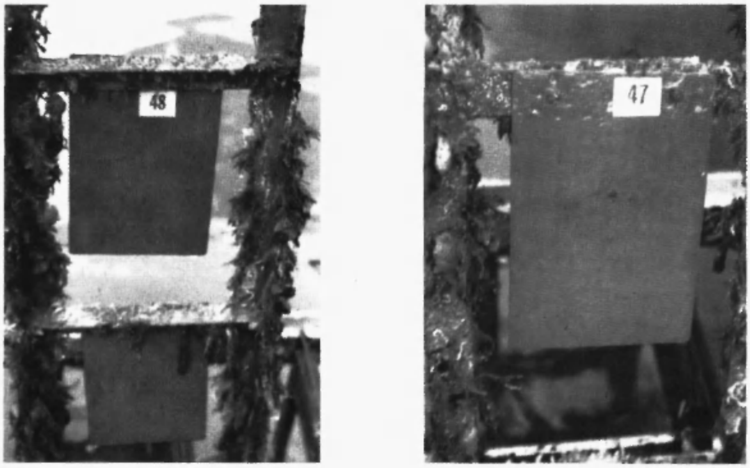
Fig. 3: Behaviour of sample D (24 hours of air exposure before immersion) in raft trial after 33 months of immersion.

(original WW rosin, 30 days of air exposure before seawater immersion) for 33 months in raft trial, which was attained with a high dry film thickness (300 μm as minimum).



4.1. WW rosin resin
Dry film thickness
required, minimum 300 μm
Efficiency, 100 %

4.2. Disproportionated WW rosin
Dry film thickness
required, minimum 250 μm
Efficiency, 100 %



4.3. Calcium resinate
Dry film thickness
required, minimum 300 μm
Efficiency, 100 %

4.4. Disproportionated calcium resinate
Dry film thickness
required, minimum 200 μm
Efficiency, 100 %

Fig. 4: Behaviour of sample D (30 days of air exposure before immersion) in raft trial after 33 months of immersion.

Disproportionated WW rosin

Advantages. This resin shows some important modifications in relation to original WW rosin. As mentioned previously, the latter is mainly formed by abietic acid and its isomers (levopimaric and isodextropimaric acids) while after its exposure to air the presence of dihydroxiabietic acid is firstly observed and when the exposure time increases (higher oxidation degree) the main component is the tetrahydroxiabietic acid /2/.

Disproportionated WW rosin is basically constituted by some of the original resin and mainly by a mixture of dehydroabietic (three double bonds), dihydroabietic (only one double bond) and tetrahydroabietic acid (without double bonds). As a consequence, the steady state dissolution rate of binders based on disproportionated WW rosin becomes practically independent of exposure time to air prior to seawater immersion, which is a very important fact from a technical and economical viewpoint in establishing drydock programs. Figs. 3.2 and 4.2 show a similar bioactivity of paint D both for 24 hours and 30 days of exposure to air prior to seawater immersion (90% and 100% of efficiency, respectively); both paints had the same dry film thickness requirement at the end of the test (33 months on experimental raft).

Disadvantages. Antifouling paints based on both WW rosin and disproportionated WW rosin as film forming resins show a high initial dissolution rate. In a first stage, the reaction between acid components of the resin and sodium and potassium ions present in seawater is responsible for the significant dry film reduction /8/ and then for the high toxicant content lixiviated /16/.

Calcium resinate

Advantages. Antifouling paints based on WW rosin show a fast reduction of resinic acid content in the outside layers of the film and a slower one in the inner ones after seawater immersion. In general, these films display an important increase of metallic resinate concentration and a marked reduction after reaching a maximum level /16/. After long immersion time, results indicate that acid materials are practically not present in the film; consequently it is possible to deduce that the film dissolution rate takes place by the solubilization of metallic resinates when the steady state is reached.

The employment of calcium resinate instead of WW rosin leads to paints which attain in service a faster dissolution steady state /8/; thus, it significantly decreases the disadvantages shown in films based on WW rosin at the beginning of seawater immersion (high dry film thickness reduction and consequently an excessive toxicant lixiviation).

In addition, when calcium resinate is selected as the soluble resin in antifouling paints, the films show in service a similar efficiency to those based on WW rosin and cuprous oxide dispersed in the absence of the acid resin /3/. Now, toxicant dispersion both in the absence or in the presence of calcium resinate and the time selected for pigment processing do not have a significant influence on the paint bioactivity. However, it markedly simplifies the paint manufacture (no exhaustive control of cuprous oxide dispersion is necessary).

Disadvantages. Films formulated with calcium resinate as soluble resin show an increase in the binder dissolution rate similar to films based on WW rosin when they are exposed to air prior to seawater immersion, consequently causing similar damage (economic loss and unnecessary marine pollution), Tables III and IV. Fig. 3.3 and 4.3 display the biocidal capacity of sample D for 24 hours and 30 days of air exposure prior to seawater immersion, respectively; dry film thickness required as minimum for 33 months on the raft is significantly higher when the painted panel was exposed to air for 30 days.

Disproportionated calcium resinate

Advantages. This resinous material combines the good properties which characterize WW rosin, disproportionated WW rosin and calcium resinate as soluble film former. Thus, antifouling paints formulated with disproportionated calcium resinate achieve a fast dissolution steady state without lixiviating unnecessary toxicant for the first stage of immersion. Binder dissolution rate (dry film thickness diminution) becomes practically independent of exposure time to air before immersion and the reaction between divalent ions and some acid components of binder during paint manufacture, which modifies the paint composition and then the film bioactivity on service, is negligible. Figs. 3.4 and 4.4 show the excellent biocidal behaviour (100 % of efficiency in both cases) corresponding to paint D, with 24 hours and 30 days of air exposure before seawater immersion, for 33 months on the raft. Paints manufactured with this resinous material are the most convenient from the technical, economical and ecological viewpoints.

Disadvantages. Disproportionated calcium resinate does not show relative disadvantages according to variables considered in this study.

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