

PRELIMINARY SHIPS' TRIALS OF
CHLORINATED RUBBER ANTIFOULING PAINTS*

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SUMMARY*

This research had as its chief target prolongation of intervals of drydocking normally required for maintenance control of corrosion and fouling.

In previous stages, the authors have developed antifouling oleoresinous formulations of high toxicity. The present work was aimed to obtain effective antifouling paints based on a chlorinated rubber binder.

Two series of ships' trials were planned applying the paints on the hull of destroyers of the Argentine Navy.

Different Rosin WW/chlorinated rubber ratios (1/1 and 2/1, by weight) were tested to establish the best matrix solubility in sea water. Also the importance of the total toxicant content on the bioactivity of the film, the toxicant/extender ratio and the use of different plasticizers were other parameters studied.

The tested paints were applied over oleoresinous anticorrosive systems, with and without intermediate paints (phenolic varnish-chlorinated rubber type).

Variables of hull painting are the location of the panels in the ships, the time of immersion and the number of periods of high settlement (spring-summer) included in the tests.

The chlorinated rubber antifouling paints studied in this paper were all of the soluble matrix type. The dissolution of Rosin WW was regulated by the presence of chlorinated rubber and the plasticizer (tricresyl-phosphate, chlorinated paraffin or chlorinated biphenyl) allows the release of toxic material and its action on the animal and vegetable organisms of fouling.

It will be noticed that:

a) The different solubility of the matrices does not influence on the bioactivity of the tested paints, in the experimental conditions considered.

b) The amount of bioactive material which varies largely in the different samples of each series (between 50 and 10 per cent, by weight) does not influence on the fouling attachment. The paints with minimum toxicant content were practically not fouled after immersion periods from 9 to 23 months.

c) The plasticizers used allow to obtain antifouling products with similar behaviour, for the tested toxicant levels and matrix

solubilities.

Some of the antifouling paints tested show poor adhesion at the end of the immersion period, when applied over the oleoresinous anticorrosive paint employed by the Navy. For this reason, in a second series of experiments, an intermediate coat was used.

The results obtained show that the useful life of the paints can be extended well beyond two years, comprise up to three periods of intense fouling attachment in temperate waters. Raft tests carried out previously would seem to confirm this possibility.

It is important to establish that in the case of soluble matrix antifouling paints, durability is proportional to film thickness. In our experiences, thickness of the antifouling films ranged between 80 and 100 μm . The thickness of the coats could be increased modifying the thixotropic characteristics of the paints.

* Rascio, V., Giudice, C. A., Benítez, J. C. and Presta, M.- Preliminary ships' trials of chlorinated rubber antifouling paints. CIDEPINT-ANALES, 1981, 57-73.

INTRODUCTION

Up to now, antifouling paints have been the most adequate method of controlling the settlement of organisms on ships'hulls.

In practice, their main drawback is the loss of toxicant that takes place during navigation and which does not have an effective action on fouling, as this adheres only when the ship is anchored in port or when it navigates at speeds below 4-5 knots. For this reason it has not been possible so far to obtain products whose effectiveness endures for periods of more than two or three years. This protection period is shorter than that of modern anti-corrosive painting systems for the underwater part of the hull.

The enlargement of the intervals between drydockings and the maintaining of vessels free from corrosion and fouling problems are the current targets of technological research in this subject.

In previous stages the authors have developed antifouling formulations of the oleoresinous type of high toxicity. They were determined by means of tests on ships (¹, ²) and experimental rafts (³, ⁴, ⁵).

The studies currently underway are aimed to obtain antifouling paints based on a chlorinated rubber binder, which show not only great effectiveness and bioactivity, but also excellent adhesion on marine anticorrosive primers prepared with different pigments.

Chlorinated rubber resin is being now used in the paint industry particularly, because the film, when correctly plasticized, has excellent resistance to chemical agents, the paints are easy to apply and the film dries quickly. In the case of anticorrosive formulations, chlorinated rubber paints provide an excellent barrier effect against water and oxygen.

VARIABLES STUDIED

On the basis of previously obtained results on panels exposed on experimental rafts (⁶), two series of tests were planned, the first one on the hulls of three destroyers and the second on

two ships, a light destroyer and a destroyer.

This preliminary report refers only to the results of the first series of tests.

Paints of different chlorinated rubber/Rosin WW ratios were tested mainly to establish the solubility of the matrix in sea water, the importance of the total toxicant content on the bioactivity of the film, the toxicant/extender ratio and the use of different plasticizers.

In order to reduce the test variables to a minimum, four of the vessels used were destroyers of the same type, which have similar operational and speed characteristics and navigation and port anchoring periods. On the other hand, the light destroyer is a vessel that navigates during shorter periods.

The aforementioned vessels are usually anchored at Belgrano's Harbour (38°58' S, 62°06' W) and navigate in the South Atlantic. The light destroyer is usually anchored at Mar del Plata's Port (38°08' S, 57°31' W) and is a support vessel for the ships and submarines that operate from the latter harbour.

The tested paints were applied over oleoresinous anticorrosive systems, with and without the use of intermediate paint (phenolic varnish-chlorinated rubber type).

1. COMPOSITION VARIABLES

a) Toxicant content

Cuprous oxide was used as fundamental toxicant; zinc oxide was employed as reinforcing toxicant in all the samples.

The cuprous oxide content in the different formulations (table 1) varies between 54,4 and 10,9 per cent, w/w, on the paint. Four of the samples have high toxicant level (paints 1, 2, 6, 7 of each series), another four can be considered as having a medium level of bioactive material (samples 3, 4, 8, 9). Finally, the samples 5 and 10 are of low content.

b) Extender content

Reduction of toxicant was carried out using an extender. Calcium carbonate (whiting) was employed due to the excellent results obtained in previous experiments (1, 2, 7, 8). The different formulations have whiting contents which vary between 0 and 48 per cent, w/w, on the paint. Extender and zinc oxide were milled during 24 hours and cuprous oxide only 3 hours.

TABLE I.- COMPOSITION OF THE ANTIFOULING PAINTS TESTED (g/100 g)

Paints*.....	1	2	3	4	5	6	7	8	9	10
Cuprous oxide....	54,4	43,5	32,6	21,7	10,9	54,7	43,7	32,8	21,9	10,9
Zinc oxide.....	5,4	4,3	3,3	2,2	1,1	5,4	4,4	3,3	2,2	1,1
Calcium carbonate	-	12,0	23,9	35,9	47,8	-	12,0	24,0	36,0	48,1
Plasticizer**....	3,9	3,9	3,9	3,9	3,9	3,9	3,9	3,9	3,9	3,9
Binder (solids)..	13,4	13,4	13,4	13,4	13,4	13,5	13,5	13,5	13,5	13,5
Solvents.....	22,9	22,9	22,9	22,9	22,9	22,5	22,5	22,5	22,5	22,5

* Paints 1/5, Rosin WW/chlorinated rubber ratio 1/1; paints 6/10, Rosin WW/chlorinated rubber 2/1

** Tricresyl-phosphate (ARA "Bouchard", samples 1/10); chlorinated paraffin 42 per cent (ARA "Stor-
ni, paints 11/20); chlorinated biphenyl (ARA "Seguí", paints 21/30).

c) *Matrix solubility*

The bioactivity of the antifouling paints is based on the solubility of Rosin WW in sea water of pH 8,0-8,2. As a result of this dissolution a thin layer with high toxicant concentration is formed closely connected with the painted surface, that is lethal to fouling organisms.

The dissolution speed of Rosin WW is controlled in our formulations by using chlorinated rubber 20 cP adequately plasticized. Rosin WW/chlorinated rubber 1/1 and 2/1 ratios have been tested (paints 1 to 5 and 6 to 10, respectively, in each series). The last ratio is the one that provides the matrix of highest solubility.

d) *Influence of the type of plasticizer*

The chlorinated rubber films were very brittle and have poor adhesion, thus it is necessary to incorporate plasticizers in the formulations.

The type and chemical characteristics of the plasticizer can influence the following properties: flexibility, chemical resistance of the film, permeability to water and oxygen, etc. Referring to antifouling paints only flexibility is important, thus allowing the use of different types of plasticizers.

The paints of the first series (ARA "Bouchard") were plasticized with tricresyl-phosphate; chlorinated paraffin 42 per cent was used in the second series (ARA "Storni") and chlorinated biphenyl in the third series (ARA "Seguí"). Tricresyl-phosphate can be considered as a saponifiable type plasticizer; the other two are of the inert type.

All the plasticizers employed are compatible with the two resins used in the formulations (Rosin WW and chlorinated rubber).

It is necessary to point out that the chlorinated biphenyl is a toxic substance. It was employed in this work considering the scientific aspect and the authors wish to make clear that they do not promote its use.

2. VARIABLES OF HULL PAINTING

a) *Selected vessels and location of the panels*

The tests which are subject matter of this report were carried out on the aforementioned destroyers (ARA "Bouchard", "Storni" and "Seguí").

As it was previously mentioned, the ARA "Bouchard" navigated during the experimental period in the South Atlantic. It was

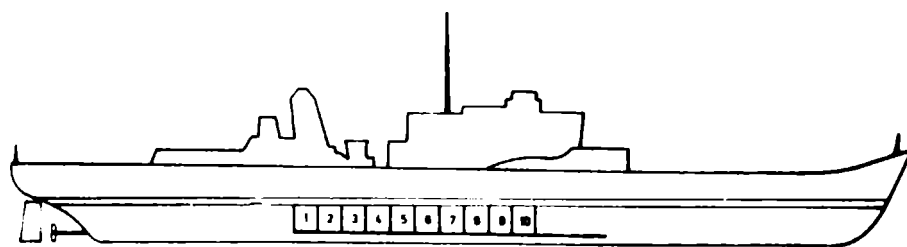


FIG. 1.—Order of the panels painted on the starboard side of the destroyer ARA "Bouchard" (plasticizer tricresyl-phosphate) and "Storni" (plasticizer chlorinated paraffin).

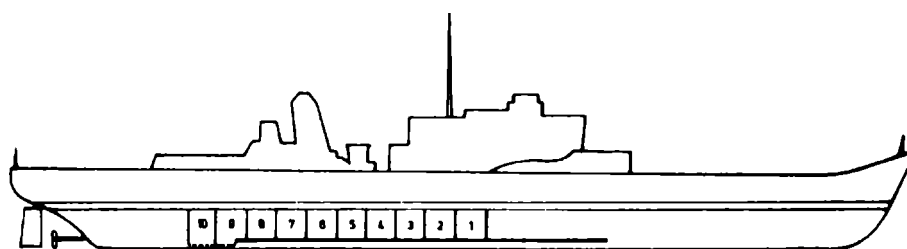


FIG. 2.—Order of the panels painted on the starboard side of the destroyer ARA "Seguí" (plasticizer chlorinated byphenil).

normally anchored at Belgrano's Harbour besides spending approximately 20 days in a port of Brazil, an area where fouling is very aggressive. The other two destroyers also navigated during rather long periods and the rest of the year remained anchored at Belgrano's Harbour.

The paint samples were placed inversely on both sides of the hull of the destroyer (port-side and starboard side). The panels so prepared covered an area of approximately 200 square meters, i.e. 10 square meters for sample.

In all the cases the application was made from the water line to the anti-roller wings. Figures 1 and 2 show the location of the painted panels on the vessels.

b) *Experimental periods*

The immersion periods of the three destroyers are shown in table II. Their length depends exclusively on the dates set by the Navy for drydocking. Normally this operation is carried out every 18-24 months. It can happen, however, that a test may have to be interrupted before the target date due to the necessity of emergency repairs. This happened in the case of the ARA "Storni", whose tests only lasted 9 months.

The destroyer ARA "Seguí", because of similar circumstances, was able to be inspected on two opportunities, 9 and 18 months af-

ter starting the test.

The ARA "Bouchard" was observed after a 23 months immersion period.

The periods of intense fouling included in each tests are also shown in table II.

T A B L E I I
IMMERSION PERIODS OF THE DIFFERENT SHIPS

	<i>Starting date</i>	<i>Completion time</i>	<i>Immersion time (months)</i>	<i>Period of intense fouling (summer)</i>
Destroyer ARA "Bouchard" ...	September 1977	August 1979	23	2
Destroyer ARA "Storni"	December 1977	August 1978	9	1
Destroyer ARA "Seguí", 1st check-up	March 1978	December 1978	9	—
Destroyer ARA "Seguí", 2nd check-up	March 1978	September 1979	18	1

PREPARATION OF THE PAINTS

The paints were prepared on a pilot plant scale using ball mills with jars of 28 liter of capacity for the dispersion of the toxicants in the binders.

Binders preparation was carried out dissolving Rosin WW and chlorinated rubber in adequate solvents and incorporating the required quantities of plasticizers to ensure good flexibility of the film.

RESULTS OBTAINED

The chlorinated rubber antifouling paints studied in this report were all of the soluble matrix type. The dissolution of Rosin WW was regulated by the presence of chlorinated rubber and the plasticizer allows the release of the toxic material and its action on the animal and vegetable organisms of fouling.

The leaching rate of the antifouling paint will be greater as the matrix becomes more soluble, but the service durability of the paint will be shorter. It is important to remark that once the necessary toxicant solubility is achieved, the leaching rate of the paint must be kept constant while toxicant reserves remain in the film. Environmental conditions are very important because a reduction in the pH of sea water can affect the solubility of Rosin WW and thus block the normal action of the antifouling formulation.

Service trials, especially on ships with long periods of navigation, ensure that the paints will be maintained in areas of low contamination which assure their normal solubilisation and the elimination of insoluble rests of the matrix (i.e. chlorinated rubber resin skeleton) or the reaction products between Rosin WW and calcium and magnesium salts present in sea water.

The above considerations explain the uniformity of the results obtained even for different toxicant concentration and experimental periods of immersion ranging from 9 to 23 months.

Except paint 20, applied on the port-side of the destroyer ARA "Storni" (settlement 1-2) in all the cases the fouling records were 0 (without settlement), 0-1 (very rare) and 1 (rare) (tables III and IV).

It will be noticed that:

a) The different solubility of the matrix (Rosin WW/chlorinated rubber ratios 2/1 and 1/1) does not influence the bioactivity of these products in the experimental conditions and all the paints have an adequate initial and constant leaching rate.

b) The amount of bioactive material which varies largely for the different samples of each series does not influence the fouling attachment. The paints with minimum toxicant content were practically unfouled.

c) The plasticizers used (tricresyl-phosphate, chlorinated paraffin and chlorinated biphenyl) allow to obtain antifouling products with similar behaviour, for the different toxicant levels and matrix solubilities employed.

TABLE III
FOULING SETTLEMENT*

	1	2	3	4	5	6	7	8	9	10
Paints.....	1	2	3	4	5	6	7	8	9	10
Destroyer ARA "Bouchard", 23 m:										
a) Port-side.....	0-1	0-1	1	1	1	0-1	0-1	1	1	0-1
b) Starboard side	1	0	0-1	0-1	1	0	0	0-1	0-1	0-1
Paints.....										
11	12	13	14	15	16	17	18	19	20	
Destroyer ARA "Storni", 9 months:										
a) Port-side.....	0	0-1	0-1	0-1	0-1	0	0	0	0	1-2
b) Starboard side	0	0	0-1	0-1	0	0	0	0	0	0-1

TABLE IV
FOULING SETTLEMENT*

Paints.....	21	22	23	24	25	26	27	28	29	30
Destroyer ARA "Se- guf", 1st. check-up, 9 months:										
a) Port-side.....	0-1	0	0	0-1	0-1	0-1	0-1	0	0-1	0-1
b) Starboard side.	0	0	0	0	0	0	0	0	0	0-1
Destroyer ARA "Se- guf", 2nd. check-up, 18 months:										
a) Port-side.....	0-1	0	0	0	0	0	0	0	0	0
b) Starboard side.	0	0	0	0	0	0	0	0	0-1	0-1

* Key of the tables III and IV: 0, without settlement (100 % efficiency); 0-1, very rare (90 %); 1, rare (80 %); 2, common (60 %); 3, very common (40 %); 4, abundant (20 %); 5, panel completely fouled (0 % efficiency).

Some of the antifouling paints tested, at the end of the immersion period, showed poor adhesion over the oleoresinous anticorrosive paint employed by the Navy. For this reason, in the second experimental stage of this work, the use of intermediate paints was considered.

The chlorinated rubber antifouling paints studied have a leaching rate for copper higher than the minimum required to ensure fouling control for ships of the Argentine Navy in periods ranging from 9 to 23 months. Navigation of the vessels at high speeds (destroyers) does not affect the durability in service of the paints. The formulations tested show good resistance to the erosive effects of water movement, the paints desintegrate slowly to permit the solubilization of the toxic material and it is not necessary to establish a compromise between toxicity and durability.

The results obtained indicate that the useful life of the paints can be extended well beyond two years, comprising up to three periods of intense attachment of fouling in temperate waters. Raft tests carried out previously would seem to confirm this possibility.

It is important to establish that in the case of soluble matrix antifouling paints, durability is proportional to film thickness. In our experiences, thickness ranged between 80 and 100 μm and it could be increased modifying the paint's binder composition with the incorporation of thixotropic substances.

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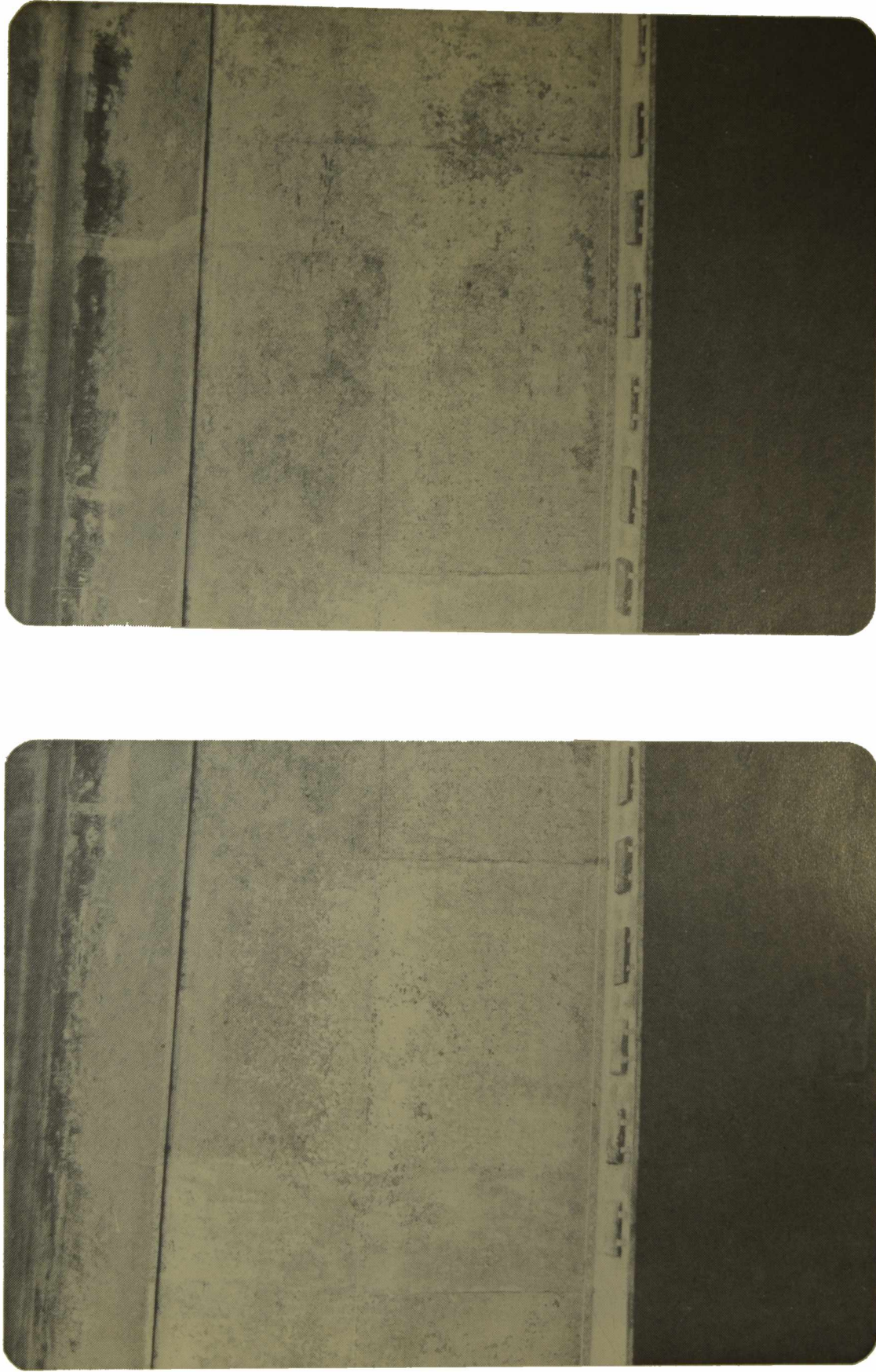


Fig. 3.- Panels corresponding to the board side of the destruction of ARA "Bouchard", plasticizer tricresyl-phosphate / 8 (right) and 23 months immersion, star-