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TOXIC ACTION OF ANTIFOULING PAINTS WITH DIFFERENT TOXICANT CONCENTRATIONS (*)

RÉSUMÉ

Une nouvelle expérience sur radeau expérimental a été effectuée dans le port de Mar del Plata durant une année (de juillet 1974 à août 1975). Cette recherche poursuivait les études entreprises sur les communautés de salissures trouvées le long des côtes argentines et leur contrôle par les peintures antisalissures.

On s'est particulièrement attaché à voir l'effet, dans la composition des peintures antisalissures, de concentrations croissantes de deux différents blancs de charge. On a fait l'essai de peintures comportant une concentration élevée de blanc de charge pour déterminer leur efficacité antisalissure, en tenant compte du coût de fabrication de la peinture.

On a utilisé deux blancs de charge différents : l'oxide ferrique et le carbonate de calcium. On a choisi le carbonate de calcium car il a la propriété d'accroître le pH de l'interface peinture - eau de mer. Il complète ainsi l'action des toxiques en vue de prévenir la fixation de salissures.

On a utilisé trois combinaisons différentes de toxiques : oxyde de cuivre - oxyde de zinc (Cu_2O-ZnO) ; oxyde de cuivre - oxyde de zinc - arsenate de mercure (Cu_2O-ZnO-AsO_4Hg_3) et oxyde de cuivre - oxyde de zinc - arsenite de cuivre (Cu_2O-ZnO-AsO_3Cu_3).

On a préparé les liants des peintures avec : colophane WW - vernis phénolique (type oléorésineux) et avec : colophane WW - résine vinylique VYHH (type vinylique).

On a entrepris l'étude avec des éprouvettes d'une dimension minimum (5 × 10 cm). Elles sont bien plus petites que celles utilisées lors des recherches précédentes. Les avantages de ces éprouvettes résident dans une meilleure utilisation des espaces disponibles sur le radeau et dans la possibilité d'essayer simultanément un plus grand nombre d'échantillons. D'autre part on peut les observer directement avec un microscope binoculaire. La taille des éprouvettes répond également aux besoins requis pour l'obtention de données biologiques.

On a essayé 8 séries de six peintures chacune ayant une concentration toxique de 100, 80, 60, 40, 20 et 0% (en poids). On a appliqué les peintures sur de l'acier sablé et des éprouvettes acryliques.

Au cours de l'expérience on a enregistré les fixations de salissures en utilisant des éprouvettes non peintes. On a recueilli des échantillons de salissures mensuellement et on les a étudiés qualitativement et quantitativement en se basant sur les données biologiques aussi bien que sur le poids et le volume des échantillons.

On a évalué les peintures tous les mois à l'aide d'une norme d'essai où 0 représente l'éprouvette sans salissures et 5 l'éprouvette entièrement recouverte de salissures. Plusieurs peintures se sont avérées de bonnes peintures antisalissures même avec des concentrations toxiques en dessous de 60% du poids du pigment.

ABSTRACT

A new investigation experience on experimental raft was carried out in the harbour of Mar del Plata during an annual period (July 1974/August 1975) as a continuation of the studies related to the fouling commuuities along the Argentine coasts, and their control by antifouling paints.

Special attention was given to the effect of increasing concentrations of two different extenders in the composition of the antifouling paints. Paints with a high extender concentration were tested to determine the antifouling efficiency. related to the paint manufacturing cost.

Two different extenders were used : ferric oxide and calcium carbonate. Calcium carbonate was selected due to its property of increasing the pH of the paint/sea water interphase, thus coupleting the action of the toxics to coutrol the fouling settlement.

Three different combinations of toxics were employed : cuprous oxide - zinc oxide (Cu_2O-ZnO) ; cuprous oxide - zinc oxide - mercurous arsenate (Cu_2O-ZnO-AsO_4Hg_3) ; and euprous oxide - zinc oxide - cuprous arsenite (Cu_3O-ZnO-AsO_3Cu_3).

The binders of the paints were prepared with rosin WW - phenolic varnish (oleoresinous type) and with rosin WW - VYHH vinyl resin (vinyl tipe).

The study was made with plates of minimum dimension (5 × 10 cm), much smaller than those used in previous research. The advantages of these plates are the best use of the raft space facilities and the possibility of test a higher number of samples simultaneously. On the other hand, they can be easily observed directly under stereomicroscope, while the size of the plates meets the biological data requirements.

Eight series of six paints each one were tested, with 100, 80, 60, 40, 20 aud 0% (in weight) of toxic concentration. The paints were applied over sandblasted steel and acrhylic plates.

Fouling settlement of the harbour was recorded during the experiment, using unpainted plates. Monthly fouling samples were obtained and qualitative and quantitative aspects of the community were established, on the basis of the biological components as well as weight and volume of the samples.

Paints were evaluated monthly using a test scale, in which 0 represents the panel without fouling and 5 the panel completely fouled. Several paints proved their antifouling properties even with toxic coucentrations under 60% in weight on the pigment.

INTRODUCTION

The first part of a technical and economic study on antifouling paint formulations was published in a previous paper [1]. The object of such investigations was to determine adequate toxicant concentrations which would prevent attachment of fouling organisms. Tests were carried out on experimental raft in the port of Mar del Plata (Argentina), where preliminary studies on hydrological and biological aspects had been already accomplished [2, 3, 4, 5, 6]. This information is essential for the correct interpretation of the behaviour and effectiveness of antifouling paints.

The results obtained up to the present moment have proved very useful in providing information on conveuient toxicant and toxicant combinations to be applied, on the type and concentration of extender to be added, and finally, on the solubility properties of the binders employed [7, 8, 9, 10, 11, 12, 13].

Special consideration has been given to the effect of pH on the interphase paint film-sea water, comparing the behaviour of several extenders such as calcium carbonate, among others. The latter gives pH values above 8.5, tbus complementing tbe actiou of the toxicants [14].

EXPERIMENTAL

An attempt has been made to include in this study the principal parameters affecting paint formulatious, with special emphasis on type and concentration of extenders. Paints with a much higher extender content than those employed in previous investigations were tested, in order to determine safety limits in the use of this kind of pigment.

Moreover, a variation has been introduced in the experimental technique replacing the usual 30 × 40 cm plates by smaller 5 × 10 cm ones with the advautage of more raft space availability,

(*) Contribution INIDEP N°376

the possibility of testing a higher number of samples at a time and of applying complex experimental procedures.

Three toxicant combinations were used : cuprous oxide-zinc oxide (Cu_2O-ZnO), cuprous oxide-zinc oxide-mercurous arsenate (Cu_2O-ZnO-AsO_4 Hg_3) and cuprous oxide-zinc oxide-cuprous arsenite (Cu_2O-ZnO-AsO_3Cu_3). In all cases, cuprous oxide is the main toxicant, given its wide range toxicity. Zinc oxide, mercurous arsenate and cuprous arsenite act as complementary toxicauts due to their specific action on certain highly resistant organisms, such as algae and barnacles.

Ferric oxide and calcium carbonate were used as extenders. The former, being insoluble in water, is completely inert ; the latter through partial hydrolisis produces saturated solutions with pH values slightly above 8.2, which is the one for sea water in non-contaminated areas. Toxicants in these formulations were partially replaced by extenders, so as to obtain paints containing 80% toxicant and 20% extender (by weight), as well as three other samples with 60-40, 40-60 and 20-80 toxicant/extender ratio respectively. Each series of six paints was tested against a sample containing 100% toxicant and another with 0% toxicant (100% extender). In this way the toxicant/extender ratio varies widely within each series.

An oleoresinous and a vinyl type of binders were used. Both are of the soluble type ; the first one is formulated with rosin WW and phenolic varnish as plasticizer, the second one with rosin WW, vinyl resin VYHH (Union Carbide) and tricresylphospate. The ratio rosin WW/phenolic varnish (3/1, 5/1 in weight) and rosin WW/vinyl resin (1/1) assures an appropriate and constant leaching rate, as stated in earlier papers.

Six series of oleoresinous paints and two series vinyl paints were prepared as follows :

- Series 1 : Cu_2O-ZnO toxicant, Fe_2O_3 extender (6 samples with 100, 80, 60, 40, 20 and 0 per cent of toxicant) (table I).
- Series 2 : Cu_2O-ZnO-AsO_4Hg_3 toxicant, Fe_2O_3 extender, with the same toxicant percentages as in series 1 (table I).
- Series 3 : Cu_2O-ZnO-AsO_3Cu_3 toxicant, Fe_2O_3 extender (table I).
- Series 4 : Cu_2O-ZnO toxicant, $CaCO_3$ extender (table II).
- Series 5 : Cu_2O-ZnO-AsO_4Hg_3 toxicant, $CaCO_3$ extender (table II).
- Series 6 : Cu_2O-ZnO-AsO_3Cu_3 toxicant, $CaCO_3$ extender (table II).

These paint series belong to the oleoresinous type. Binder composition and rosin WW/plasticizer ratio are summarized in tables I and II.

- Series 7 : Cu_2O-ZnO-AsO_4Hg_3 toxicants, Fe_2O_3 extender (table III).
- Series 8 : Cu_2O-ZnO-AsO_4Hg_3 toxicants, $CaCO_3$ extender (table III).

These last two series correspond to the vinyl type and their compositions were given in table III.

TABLE I

Paints series 1 : oleoresinous binder (Rosin WW/plasticizer, 3/1) (*)

	1.1	*1.2*	*1.3*	*1.4*	*1.5*	*1.6*
Cuprous oxide	46.9	37.5	28.1	18.8	9.4	—
Zinc oxide	4.6	3.7	2.8	1.8	0.9	—
Ferric oxide	—	10.3	20.6	30.9	41.2	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	17.3	17.3	17.3	17.3	17.3	17.3
Plasticizer	5.7	5.7	5.7	5.7	5.7	5.7
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

Paints series 2 : oleoresinous binder (Rosin WW/plasticizer 5/1) (*)

	2.1	*2.2*	*2.3*	*2.4*	*2.5*	*2.6*
Cuprous oxide	41.0	33.0	25.0	17.0	9.0	—
Zinc oxide	4.1	3.3	2.5	1.7	0.9	—
Mercurous arsenate	6.4	5.0	3.6	2.2	0.8	—
Ferric oxide	—	10.2	20.4	30.6	40.8	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	19.2	19.2	19.2	19.2	19.2	19.2
Plasticizer	3.8	3.8	3.8	3.8	3.8	3.8
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

Paints series 3 : oleoresinous binder (Rosin WW/plasticizer 5/1) (*)

	3.1	*3.2*	*3.3*	*3.4*	*3.5*	*3.6*
Curpous oxcd	41.0	33.0	25.0	17.0	9.0	—
Zinc oxide	4.1	3.3	2.5	1.7	0.9	—
Cuprous arsenite	6.4	5.0	3.6	2.2	0.8	—
Ferric oxide	—	10.2	20.4	30.6	40.8	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	19.2	19.2	19.2	19.2	19.2	19.2
Plasticizer	3.8	3.8	3.8	3.8	3.8	3.8
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

(*) g/100 g.

TABLE II

Paints series 4 : oleoresinous binder (Rosin WW/plasticizer, 3/1) (*)

	4.1	4.2	4.3	4.4	4.5	4.6
Cuprous oxide	46.9	37.5	28.1	18.8	9.4	—
Zinc oxide	4.6	3.7	2.8	1.9	0.9	—
Calcium carbonate (whiting)	—	10.3	20.6	30.9	41.2	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	17.3	17.3	17.3	17.3	17.3	17.3
Plasticizer	5.7	5.7	5.7	5.7	5.7	5.7
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

Paints series 5 : oleoresinous binder (Rosin WW/plasticizer, 5/1 (*)

	5.1	5.2	5.3	5.4	5.5	5.6
Cuprous oxide	41.0	33.0	25.0	17.0	9.0	—
Zinc oxide	4.1	3.3	2.5	1.7	0.9	—
Mercurous arsenate	6.4	5.0	3.6	2.2	0.8	—
Calcium carbonate (whiting)	—	10.2	20.4	30.6	40.8	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	19.2	19.2	19.2	19.2	19.2	19.2
Plasticizer	3.8	3.8	3.8	3.8	3.8	3.8
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

Paints series 6 : oleoresinous binder (Rosin WW/plasticizer, 5/1) (*)

	6.1	6.2	6.3	6.4	6.5	6.6
Cuprous oxide	41.0	33.0	25.0	17.0	9.0	—
Zinc oxide	4.1	3.3	2.5	1.7	0.9	—
Cuprous arsenite	6.4	5.0	3.6	2.2	0.8	—
Calcium earbonate (whiting)	—	10.2	20.4	30.4	40.8	51.5
Aluminium stearate	2.5	2.5	2.5	2.5	2.5	2.5
Rosin WW	19.2	19.2	19.2	19.2	19.2	19.2
Plasticizer	3.8	3.8	3.8	3.8	3.8	3.8
Solvents	23.0	23.0	23.0	23.0	23.0	23.0

(*) g/100 g.

TABLE III

Paints series 7 : vinyl binder (Rosin WW/VYHH resin) (*)

	7.1	7.2	7.3	7.4	7.5	7.6
Cuprous oxide	52.2	41.8	31.4	21.0	10.6	—
Mercurous arsenate	7.8	6.2	4.6	3.0	1.4	—
Ferric oxide	—	12.0	24.0	36.0	48.0	60.0
Rosin WW	6.0	6.0	6.0	6.0	6.0	6.0
Vinyl resin VYHH	6.0	6.0	6.0	6.0	6.0	6.0
Tricresyl-phosphate	1.5	1.5	1.5	1.5	1.5	1.5
Metyl-isobutyl-ketone	13.5	13.5	13.5	13.5	13.5	13.5
Toluene	13.0	13.0	13.0	13.0	13.0	13.0

Paints series 8 : vinyl binder (Rosin WW/VYHH resin) (*)

	8.1	8.2	8.3	8.4	8.5	8.6
Cuprous oxide	52.2	41.8	31.4	21.0	10.6	—
Mercurous arsenate	7.8	6.2	4.6	3.0	1.4	—
Calcium carbonate (whiting)	—	12.0	24.0	36.0	48.0	60.0
Rosin WW	6.0	6.0	6.0	6.0	6.0	6.0
Vinyl resin VYHH	6.0	6.0	6.0	6.0	6.0	6.0
Tricresyl-phosphate	1.5	1.5	1.5	1.5	1.5	1.5
Methyl-isobutyl-ketone	13.5	13.5	13.5	13.5	13.5	13.5
Toluene	13.0	13.0	13.0	13.0	13.0	13.0

(*) g/100 g.

TABLE IV

Toxicant contents of the antifouling paints

	Oleoresinous binder (%)	*Vinyl binder* (%)
1. *Composition of the paint:*		
Pigment	54.0	60.0
Binder	23.0	13.5
Solvents	23.0	26.5
2. *Composition of the dry film:*		
Pigment	70.0	82.0
Binder	30.0	18.0
3. *Toxicant contents of the dry film:*		
Paints number 1	70.0	82.0
" " 2	56.0	66.0
" " 3	42.0	49.0
" " 4	28.0	33.0
" " 5	14.0	16.0
" " 6	0.0	0.0

TABLE V

Thiclness of the paint film (microns)

Paints and series	*Thickness of the primer* (μ)	*Thickness of the AF film* (μ)	*Total thickness* (μ)
1.1	225	75	300
1.2	205	75	280
1.3	185	85	270
1.4	205	85	290
1.5	150	55	205
1.6	180	60	240
2.1	160	60	220
2.2	180	60	220
2.3	160	60	220
2.4	165	55	220
2.5	175	55	230
2.6	150	50	200
3.1	175	85	260
3.2	155	85	240
3.3	185	55	240
3.4	160	60	220
3.5	160	50	210
3.6	170	50	220
4.1	170	70	240
4.2	180	90	270
4.3	180	60	240
4.4	150	60	210
4.5	200	65	265
4.6	180	60	240
5.1	190	70	260
5.2	170	50	220
5.3	180	60	240
5.4	180	60	220
5.5	190	50	240
5.6	200	60	260
6.1	165	90	255
6.2	190	60	250
6.3	175	55	230
6.4	185	55	240
6.5	170	70	240
6.6	190	60	250
7.1	150	70	220
7.2	160	90	250
7.3	140	70	210
7.4	135	85	220
7.5	160	90	250
7.6	160	70	230
8.1	130	80	210
8.2	150	70	220
8.3	180	70	250
8.4	150	80	230
8.5	180	80	260
8.6	150	90	240

LOCALITY, SUBSTRATE CONDITIONS AND REFERENCE PLATES

Experiments were carried out on a raft anchored in the port of Mar del Plata, as stated at the beginning of this paper. Nine frames were used, eight for painted plates and one carrying inert plates.

Steel plates 3 mm thick and plastic panels (achrylic) 5 mm thick were used in the paint tests. Both types of panels were previously sandblasted in order to provide a suitable surface for paint application. Steel plates were protected with a vinyl wash-primer and three coats of anticorrosion paint; plastic plates were painted only with the anticorrosion paint. Finally, two coats of antifouling paint was applied on each panel (thickness is given in table V).

The achrylic plates were used in order to eliminate corrosion due to edge effect and the consequent alteration of the antifouling paint film.

The six plates belonging to each paint series were mounted on a panel of the same material (30 × 40 cm). Each frame contained two panels of this kind and was placed at a depth of 1-2 m. In this way all the plates are situated close enough to ensure similar conditions but no interaction between different paints occurs (fig. 1).

Each plate is separated from the base panel by rubber rings 1 cm thick. In all cases the base panel was painted in the same way as the corresponding plates and the paint with the highest toxicant content was used in each case. This prevented fouling attachment along the experimental period and eventual colonization of the plates by succesive epibiosis processes [15].

The inert achrylic plates for reference fouling samples were mounted in the same way as the painted ones. Twelve of these plates were placed at the same depth as the others and one was removed each month for laboratory observations.

(A) (B) (C) (D) (E) (F)

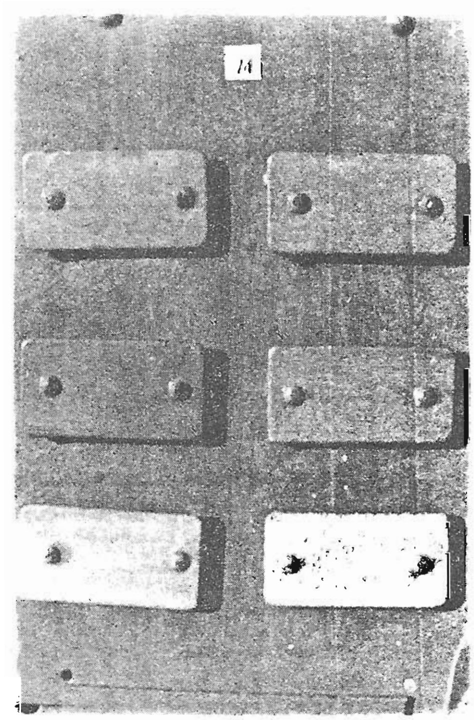


Fig. 1

Six test plates corresponding to a series of antifouling compositions, supported on a 30×40 cm panel. (A) 100% toxicant; (B) 80%; (C) 60%; (D) 40%; (E) 20%; and (F) 0%

EVOLUTION OF THE FOULING COMMUNITY ON INERT PLATES

In this chapter, references of the main aspects of the fouling community evolution on inert plates are given for an annual period (fig. 2 and 3).

Registered species are shown in table VI.

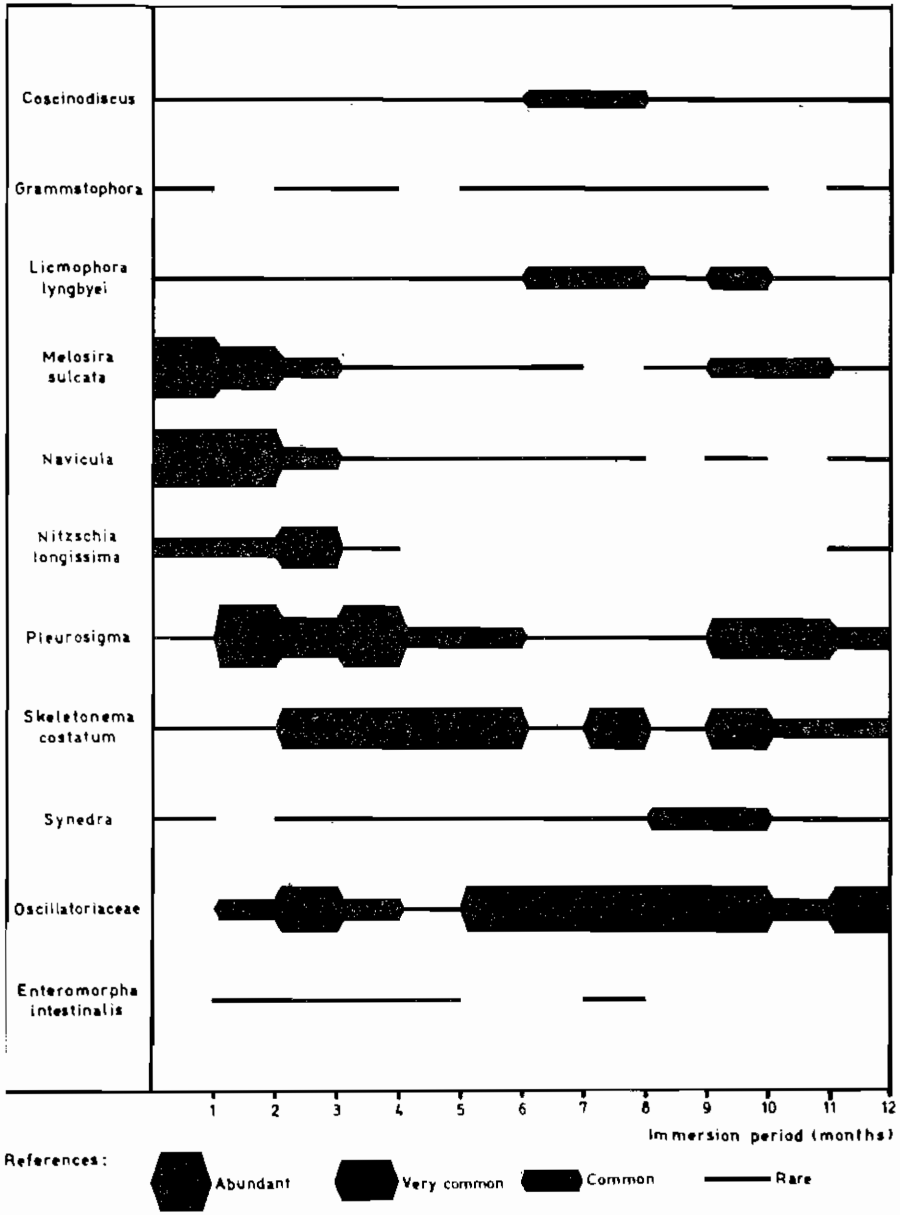


Fig. 2

Settlement and evolution of main fouling organisms on long term inert plates (Mar del Plata's harbour, 20-7-74/20-7-75)

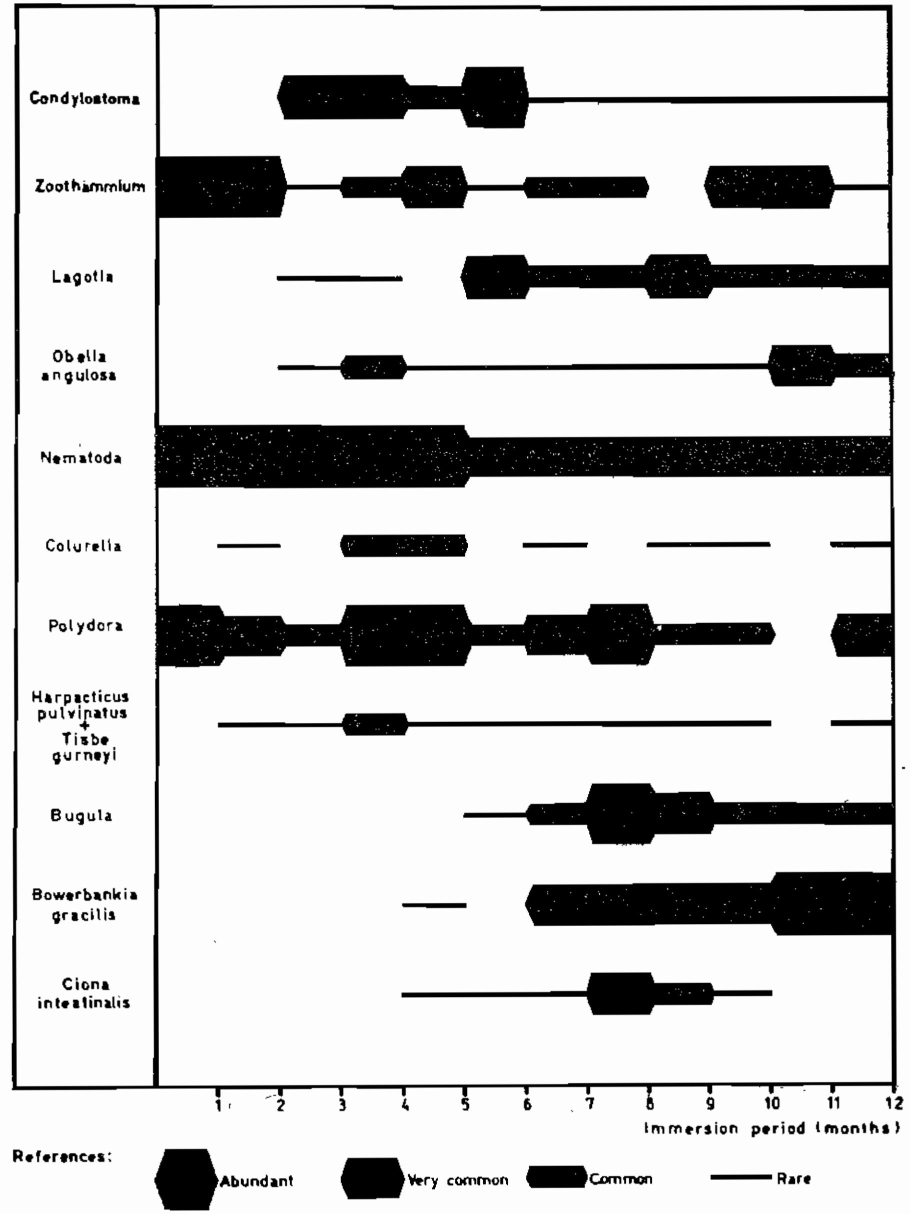


Fig. 3

Settlement and evolution of main fouling organisms on long term inert plates (Mar del Plata's harbour, 20-7-74/20-7-75)

TABLE VI

List of the fouling organisms settled during the experience (*)

	Immersion period (months)											
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
Diatomeae												
Achnantes sp.						R						
Biddulphia chinensis									R			
Biddulphia roperiana		R										
Chaetoceros sp.		R										
Coscinodiscus sp.	R	R	R	R	R	R	C	C	R	R	R	R
Grammatohora sp.	R		R	R		R	R	R	R	R		R
Licmophora lyngbyei	R	R	R	R	R	R	C	C	R	C	R	R
Melosira sulcata	A	VC	C	R	R	R	R		R	C	C	R
Navicula spp.	A	A	C	R	R	R	R	R		R		R
Nitszchia longissima	C	C	VC	R								R
Nitszchia seriata		R			R							R
Pleurosigma sp.	R	A	VC	A	C	C	R	R	R	VC	VC	C
Pinnularia sp.										R		
Rhizosolenia sp.			VC	C		R				R		
Skeletonema costatum	R	R	VC	VC	VC	VC	R	VC	R	VC	C	C
Stephanopyxis sp.									R			
Synedra sp.	R		R	R	R	R	R	R	C	C	R	R
Thalassionema nitzschiaides							R			R		
Triceratum sp.					R		R	R	R			
Cyanophita												
Oscillatoriaceae		C	VC	C	R	VC	VC	VC	VC	VC	C	VC
Chroococcaceae						C						
Clorophyta												
Enteromorpha intestinalis		R	R	R	R		R					
Rodophyta												
Polysiphonia sp.		R										
Protozoa												
Acineta sp.	VC	R							R	R		
Colpidium sp.	C	VC		VC							R	R
Condylostoma sp.			VC	VC	C	A	R	R	R	R	R	R
Cothurnia sp.									R			
Exuviaella sp.	R									R	R	R
Favella sp.					C	R		R	C			
Bolivina sp.								R				
Elphidium sp.			R			R			R			
Lacrymaria sp.							R		R	C	R	R
Lagotia sp.			R	R		VC	C	C	VC	C	C	C
Peridinium sp.	R											
Tintinnopsis sp.	R		R	R	VC	R	C	R	C			
Vorticella sp.		R				R	VC	VC	C	C		R
Zoothamnium sp.	A	A	R	C	VC	R	C	C		VC	VC	R
Coelenterata												
Obelia angulosa			R	C	R	R	R	R	R	R	VC	C
Tubularia crocea								R				
Nematoda	A	A	A	A	A	VC	VC	VC	VC	VC	VC	VC
Rotatoria												
Colurelle sp.		R		C	C		R		R	R		R
Annelida												
Terebollidae									R			
Dorvillea sp.							R		R	R	C	C
Eulalia sp.								R				R
Polydora ligni	A	VC	C	A	A	C	VC	A	C	C		VC
Polynoidae indet										R		
Syllis sp.										R		
Mollusca												
Mytilus platensis											R	
Tenellia pallida										R	R	C
Crustacea												
Balanus amphitrite							C	R	R			
Balanus trigonus								R				R
Cyrtograpsus angulatus								R				
Tisbe gurneyi + Harpacticus pulvinatus		R	R	C	R	R	R	R	R	R		R
Bryozoa												
Bugula sp.						R	C	A	VC	VC	VC	VC
Bowerbankia gracilis					R		VC	VC	VC	VC	A	A
Tunicata												
Ciona intestinalis					R	R	R	VC	C	R		

(*) On the inert plates.

Key of the table: A : Abundant ; VC : Very common ; C : Common ; R : Rare.

TABLE VII

Fouling settlement on inert test plates (5 × 10 cm) at mar del Plata's Harbour, 20-7-74/20-7-75

Immersion period (months)	*Number of species*	*Fouling volume (ml)*		*Fouling wet weight (g)*		*Fouling dry weight (g)*	
		Front	*Back*	*Front*	*Back*	*Front*	*Back*
1	17	2.8	0.2	1.42	0.11	0.174	0.013
2	21	21.2	2.3	9.64	1.05	1.106	0.120
3	21	31.4	5.6	16.03	2.89	1.702	0.304
4	22	36.9	4.1	22.50	2.50	2.239	0.249
5	22	82.8	9.2	78.11	8.68	5.525	0.614
6	25	16.5	5.5	6.75	2.25	0.777	0.259
7	27	57.0	2.0	17.10	0.63	1.902	0.067
8	29	193.2	16.8	167.44	14.56	15.224	1.324
9	31	56.1	9.9	34.08	6.01	2.360	0.416
10	30	60.4	10.6	28.30	4.96	3.012	0.529
11	31	63.2	15.8	40.24	10.06	2.899	0.725
12	29	62.0	11.0	39.02	6.92	3.837	0.681

TABLE VIII

Fouling settlement of the painted plates (scale 0 to 5) (*)

Paints	*Immersion period (months)*			
	3	*6*	*9*	*12*
1.1	0	1	1-2	1-2
1.2	0	1	1-2	1-2
1.3	0-1	0-1	0-1	1
1.4	1-2	1-2	2	2
1.5	3	3	3	3
1.6	5	5	5	5
2.1	0	0	0	0
2.2	0	0	0	0
2.3	0	1	1-2	2
2.4	0-1	0-1	0-1	0-1
2.5	1-2	2	2	2-3
2.6	3-4	5	5	5
3.1	0	0	0	0-1
3.2	0	0-1	0-1	1-2
3.3	0-1	0-1	0-1	1-2
3.4	1	1	1	2
3.5	2	2	2	2-3
3.6	4-5	5	5	5
4.1	0	0	0-1	0-1
4.2	0	0-1	1	1
4.3	0	0-1	1-2	1-2
4.4	0-1	1	2-3	2-3
4.5	1-2	2	2	2
4.6	4-5	5	5	5
5.1	0	0	0	0
5.2	0	0	0	0
5.3	0	0	0	0
5.4	0-1	0-1	0-1	1
5.5	1	1	2	2
5.6	5	5	5	5
6.1	0	0	0	0
6.2	0	0	0	0
6.3	0	0	0	0
6.4	0	0	0	0
6.5	1	1	1	1
6.6	4	5	5	5
7.1	0	0	1	1-2
7.2	0	0	0	0
7.3	0	0	1-2	1-2
7.4	0	0-1	2	2
7.5	1	1	2-3	2-3
7.6	4	5	5	5
8.1	0	0	0-1	0-1
8.2	0	0	0-1	0-1
8.3	0	0	0-1	0-1
8.4	0-1	0-1	0-1	0-1
8.5	0-1	0-1	1-2	2
8.6	4	5	5	5

Key of the table: 0 (without settlement); 1 (rare); 2 (common); 3 (very common); 4 (abundant); 5 (plate completely fouled).

Note : Fouling settlement was registered monthly; for simplicity, in this table only are presented values corresponding to 3, 6, 9 and 12 months immersion.

INITIAL THREE-MONTH PERIOD (20-7-74/10-20-74)

Colonizing processes during the first month of immersion are similar to those previously observed in the area. The fouling volume during this period is low (2.8 ml). Fouling organims do not cover the entire surface of the plates, and form a typical slime film composed mainly of diatoms (*Melosira sulcata* and *Navicula* sp., among others) and the protozoan *Zoothamnium* sp. as well as abundant nematodes.

The only macrofouling organism present is *Polydora ligni* (young specimens) and its tubes contribute to consolidate the slime film. In this month the lowest specific diversity was observed due to the short immersion period and to the fact that the experience was started during the winter season.

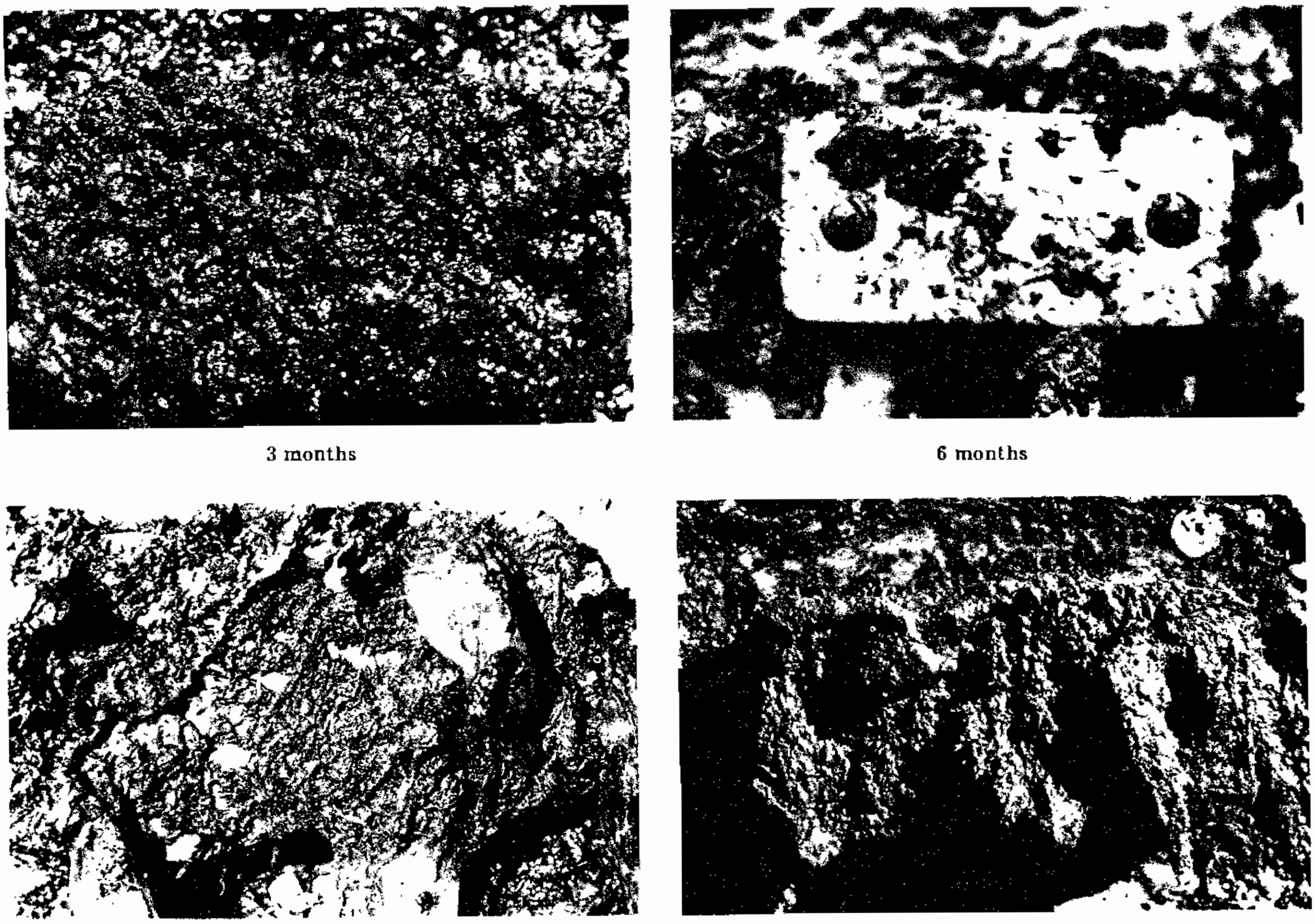
After the first month, fouling volume increases markedly, reaching 21.2 ml on the sixtieth day. This fact is due mainly to the high density and size of *Polydora* specimens, which cover the substrate completely, as well as to other species that contribute to increase the specific diversity of the young community. Harpacticoid copepods and superior algae are observed for the first time, though in small amounts. Among the microfoulers, *Melosira sulcata, Pleurosigma* sp., *Navicula* sp. and *Zoothamnium* sp. are the dominant species.

At the end of the third month, fouling volume increases one more (31.4 ml). There is no evident change in macrofouling composition, while thickness of the fouling cover is practically doubled through growth of *Polydora* tubes (fig. 4). Many of the tubes are empty, as most of these colonizers have reached the end of their life-cycle. Colonies of the hydroid *Obelia angulosa* appear for the first time. Among the microfoulers, *Zoothamnium* decreases in number, while blue-green algae increases and there is a clear dominance of diatoms (*Pleurosigma, Rhizosolenia, Nitzschia longissima, Skeletonema costatum*, etc.).

SECOND THREE-MONTH PERIOD (20-10-74/20-1-75)

On the fouth month of immersion the community presents similar characteristics to those observed on the second month. Its most outstanding feature is the clear dominance of *Polydora*, which has increased so much in density that the tubes now grow perpendicular to the plate surface due to lack of space. Most of these tubes are occupied by specimens of small and medium size. The fouling volume has slightly increased. (36.9 ml) and new specimens of *Enteromorpha intestinalis* of small size are now present. These do not thrive owing to unfavourable conditions at the depth at which attachment has taken place. The colonies of *Obelia* have grown bigger and more numerous, in spite of the fact that specimens have not yet reached sexual maturity. Among animal microfoulers, while *Zoothamnium*, is comparatively less frequent. *Pleurosigma* and *Skeletonema* are the most important diatoms.

During the fifth month, the fouling community shows great development, with the formation of a layer 25 mm thick consisting mainly of *Polydora* tubes (total volume 82.2 ml). Most of the Polydora specimens are of a large size and present mature gonads. Many of the *Obelia* colonies have completed their life-cycle and a large number of epizoic forms are attached to their branches, including egg masses of *Tenellia pallida*. Colonies of *Bowerbankia gracilis* appear to the first time and contribute to consolidate the whole fouling layer. Young specimens of *Ciona intestinalis* are also present. Among microfoulers, *Zoothamnium* has greatly increased and diatoms are less abundant, probably as a result of spatial competence with *Polydora* and grazing action of the latter.



3 months

6 months

9 months

12 months

Fig. 4
Aspect of the inert plates after 3, 6, 9 and 12 months of immersion

On the sixth month, the *Polydora*-dominated community has completed the cycle and the fouling layer is in the process of dettachment. Portions of the expérimental substrate become partly exposed (fig. 4) and the fouling volume consequently decreases (16.5 ml).

Ciona specimens have grown in size and the presence of *Bugula* sp. is recorded for the first time. Observations under microscope reveal the dominance of diatoms and blue-green algae in the process of recolonization.

THIRD THREE-MONTH PERIOD (20-1-75/20-4-75)

At the end of the seventh month of immersion, the plates have been colonized by a new stock of *Polydora* specimens. This species tends to cover the whole plate surface, either through direct attachment or as a result of epibiosis on *Balanus amphitrite* among others.

Bugula and *Bowerbankia* are also present during this month, while *Ciona*, after completing its life-cycle has disappeared. However, juvenile forms belonging to a second colonizing cycle can be observed.

Among microfoulers, nematodes are densely represented and *Vorticella* is numerically more important than *Zoothamnium*. Blue green algae increase in number while diatoms are poorly represented (*Coscinodiscus* sp., *Licmophora lyngbyei*, etc.).

At the end of the eighth month of immersion, fouling volume reaches its highest value (193.2 ml). This is mainly due to the presence of *Polydora*, *Ciona*, *Balanus amphitrite*, *B. trigonus*, *Bugula*, *Bowerbankia*, *Obelia* and *Tubularia crocea*. The fouling layer 22 mm thick is characterized by the abundance of *Polydora* tubes which are empty in a high percentage.

Microfouling is similar in composition to that observed in the previous month and its volume is insignifieant with respect to the total value.

The empty tubes of Polydora indicate their imminent dettachmeut, which finally begins on the nineth month (fig. 4). The fouling volume consequently drops to 56.1 ml. The remaining macrofoulers show little variation, except for *Ciona*, that increases remarkably in size (4 cm).

FOURTH THREE-MONTH PERIOD (20-4-75/20-7-75)

The process of dettachment continues during the tenth month. *Ciona* specimens having completed their life-cycle, are no longer present in the fouling samples. A few *Polydora* tubes can be observed, and *Bowerbankia* colonies tend to cover densely most of the exposed substrate. Fouling volume suffers little variation (60,4 ml).

At the beginning of the eleventh month, *Polydora* has completely disappeared from the fouling community. During this stage *Bowerbankia* reaches its maximnm density and becomes the dominant speeies. *Obelia* also increases in number and is once again associated with *Tenellia*. The main macrofoulers are *Zoothamnium*, nematodes and *Pleurosigma*. The total fouling volume is now 63.2 ml.

At the end of one year of immersion, the colonizing process of *Polydora* recommences and a clear spatial competition with *Bowerbankia* takes place. Fouling volume remains constant.

Figure 4 shows the plates after three, six, nine and twelve months of immersion.

The evolution of the fouling community along the studied period is clearly marked by the dominance of *Polydora*. This tubeworm was recorded in the area since our first researches in 1966, but had never played a significant role in fouling dynamics of the port of Mar del Plata. However it has recently become very abundant and its seasonal settlement now covers a longer period. This is associated with pollution phenomena in the port area and has been favoured by the species adaptability to polluted conditions. On the other hand, competing populations have either deeliued or disappeared.

These facts constitute a serious problem in fouling control, since *Polydora* is quite resistant to toxicants of common use. Moreover the tubes offer an adequate substrate for the settlement of epizoic organisms at a distance from the paint film and out of the range of the toxicant action of the pigment.

ANTIFOULING PAINTS PERFORMANCE

With regard to evaluation of antifouling paint performance, the technique based on a settlement scale from 0 to 5 employed in earlier experiences was applied. This scale is based on direct observation of the plates, as well as on a photographic control during the test and on accurate laboratory analysis at the end of the exposure period.

In addition, the fouling settlement along an annual period was quantitatively evaluated on the basis of its volume, wet weight and dry weight. Qualitative information of species composition and abundance was also obtained. These data are summarized in table IX and shown graphically in figures 5, 6, 7.

Both methods evidences good correlation, and fouling volume constitutes an excellent complement of the classical evaluation scale method.

The *different factors affecting antifouling paint action* will be separately analyzed.

TABLE IX

Results obtained on antifouling paints after an annual immersion period at Mar del Plata (20-7-74/20-7-75)

Paints		*Number of species*	*Fouling settlement*	*Fouling volume (ml)*	*Fouling wet weight (g)*	*Fouling dry weight (g)*
Series 1 : Cu_2O	1	13	1-2	6.0	3.09	0.638
ZnO	2	13	1-2	4.7	3.66	0.401
Fe_2O_3	3	11	1	3.9	3.89	0.361
	4	22	2	13.0	11.32	1.251
	5	18	3	26.0	17.01	1.964
	6	27	5	49.0	28.86	3.708
Series 2 : Cu_2O	1	10	0	3.5	2.39	0.237
ZnO	2	6	0	3.0	2.05	0.248
AsO_4Hg_3	3	17	2	16.0	11.79	1.718
Fe_2O_3	4	19	1	6.0	8.69	1.004
	5	19	2-3	12.0	8.23	0.950
	6	25	5	71.0	42.67	6.023
Series 3 : Cu_2O	1	10	0-1	6.2	5.01	0.565
ZnO	2	14	1-2	7.5	6.47	0.638
AsO_3Cu_3	3	18	1-2	9.5	7.06	0.668
Fe_2O_3	4	24	2	17.0	12.86	1.337
	5	24	2-3	25.0	18.87	2.188
	6	29	5	46.0	40.66	5.107
Series 4 : Cu_2O	1	11	0-1	2.8	2.19	0.296
ZnO	2	9	1	1.7	1.93	0.210
$CaCO_3$	3	11	1-2	3.0	3.10	0.453
	4	19	2-3	11.0	9.83	1.213
	5	19	2	6.5	4.83	0.671
	6	23	5	28.0	22.16	2.714
Series 5 : Cu_2O	1	7	0	3.1	2.94	0.305
ZnO	2	4	0	3.5	4.06	0.366
AsO_4Hg_3	3	7	0	2.7	2.89	0.258
$CaCO_3$	4	17	1	5.8	4.70	0.634
	5	18	2	16.5	16.59	1.661
	6	23	5	57.0	41.00	6.159
Series 6 : Cu_2O	1	8	0	4.5	2.28	0.347
ZnO	2	7	0	3.5	2.39	0.281
AsO_3Cu_3	3	10	0	2.5	2.39	0.171
$CaCO_3$	4	11	0	3.2	2.60	0.204
	5	13	1	2.8	2.30	0.255
	6	26	5	57.0	37.26	3.876
Series 7 : Cu_2O	1	16	2	6.0	5.40	0.670
ZnO	2	10	0	4.0	3.10	0.377
AsO_4Hg_3	3	23	2	13.0	9.49	1.536
Fe_2O_3	4	25	2	31.0	24.22	4.735
	5	23	2-3	12.0	6.64	0.950
	6	29	5	104.0	76.43	10.920
Series 8 : Cu_2O	1	15	0-1	7.5	6.54	0.691
ZnO	2	8	0-1	3.7	2.33	0.301
AsO_4Hg_3	3	10	0-1	3.8	1.69	0.275
$CaCO_3$	4	11	0-1	3.2	2.20	0.232
	5	25	2	20.5	14.85	1.794
	6	28	5	70.0	56.40	7.676

Note : Paints of series 1 to 6 are oleoresinous type ; series 7 and 8 correspond to vinyl type.

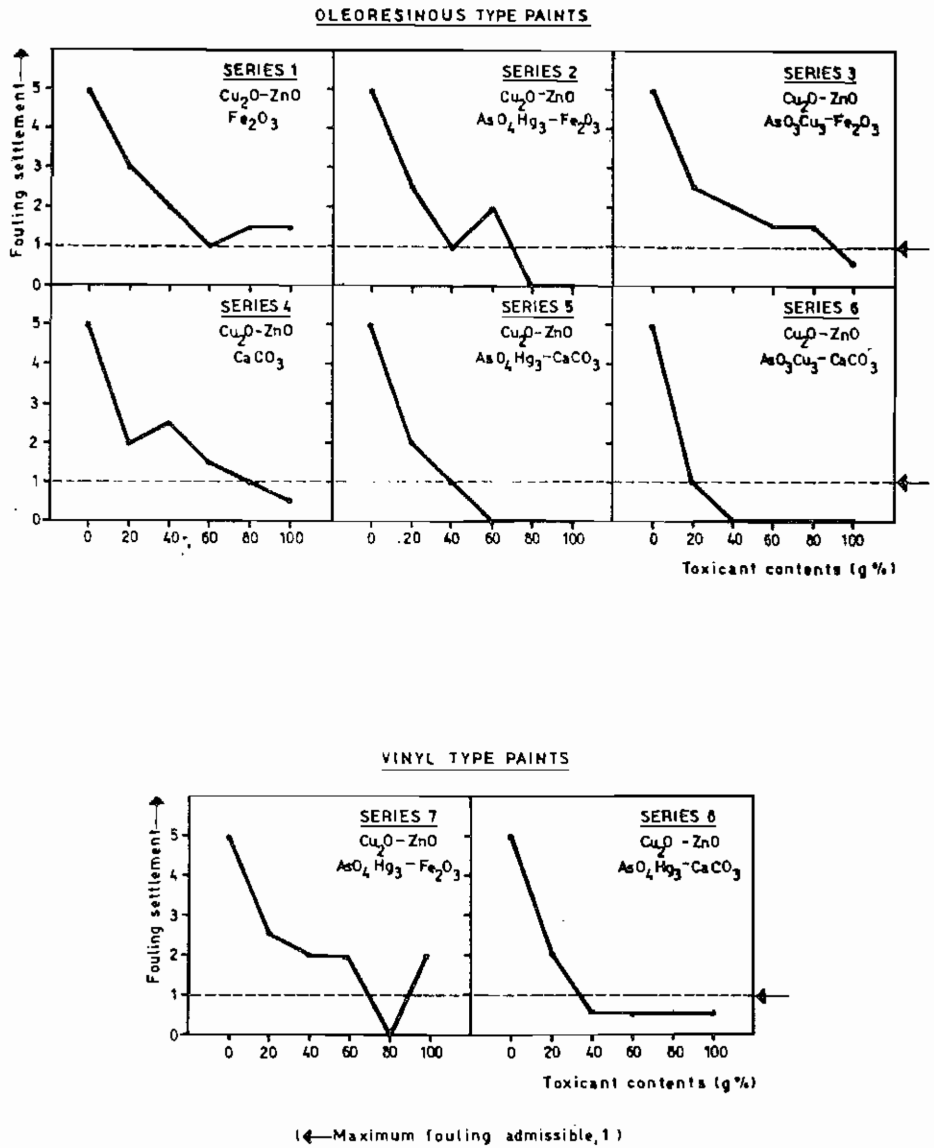


Fig. 6

Fouling rate (0-5 scale) for each pair of paints with similar toxicants and different extenders (12 month immersion period)

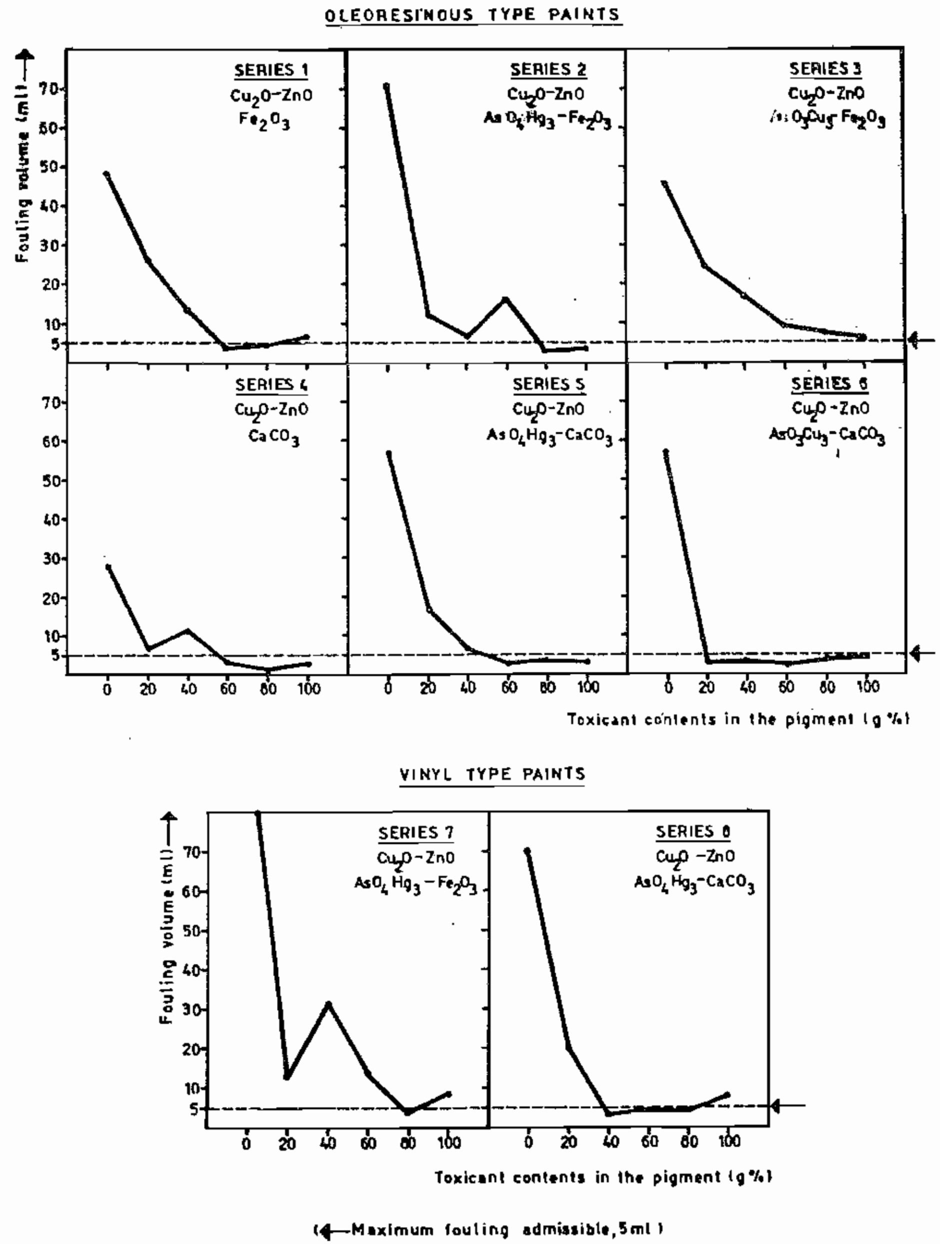


Fig. 5

Fouling rate (volume) for each pair of paints with similar toxicants and different extenders (12 month immersion period)

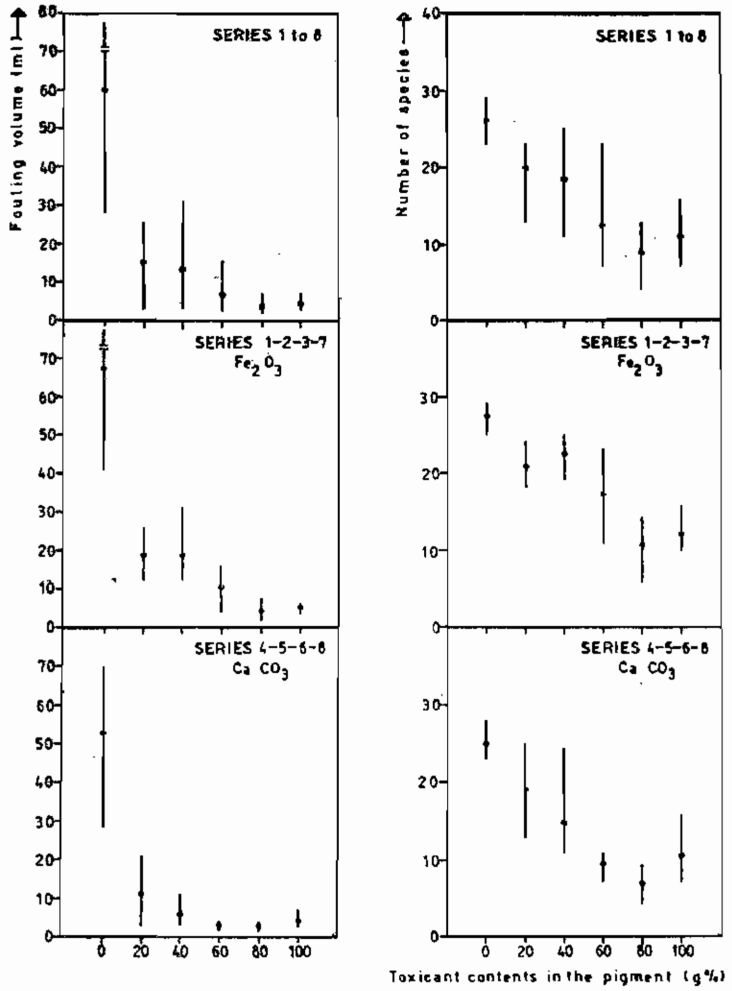


Fig. 7

Fouling rate (volume and number of species) for series of paints based on different toxicants and using as extenders ferric oxidc a1 calcium carbonate (12 month immersion period)

TOXICANT CONTENTS

The first five samples of each series of oleoresinous paints contains 70, 56, 42, 28 and 14 per cent by weight of bioactive material in the dry film, while in vinyl paints these values are slightly higher (82, 66, 49, 33 and 16) as a consequence of the lower binder content. Furthermore, in each series a non toxic reference paint was included. Paint tests comprising such a wide range of toxicant content have not been previously carried out in Argentina.

In all series, fouling settlement tends to increase with decreasing toxicant content (fig. 6). However some abnormal results are observed in series 1, 2 and 7, where paints with high toxicant content present more fouling settlement than those with less toxicant content (samples 1.1, 1.2, 2.3 and 7.1).

On the other hand, certain paint formulations (6.4, 6.5 and 8.4) present settlement values below the accepted maximum 0-1, 0 and 1 respectively) in spite of a low toxicant content. These two facts suggest that direct contact between toxicant particles is not really necessary to ensure antifouling effectiveness, as some theories propose (16, 17).

TOXICANT TYPE

A comparative analysis of the first three series (fig. 6) shows that samples containing mercurous arsenate (15% in weight relative to cuprous oxide-zinc oxide mixture, and 0.8 to 6.4% referred to the paint weight) produce the paints with the greatest bioactivity. In samples 2.1 and 2.2, fouling settlement has been 0 and in paint 2.4 fouling settlement 1 was recorded.

In series 5 and 6, both reinforcing toxicants (mercurous arsenate, cuprous arsenite) contribute in the antifouling action of the paints. Thus, in the fourth series (cuprous oxide-zinc oxide) only the first two samples fulfil standards requirements. In the fifth series (mercurous arsenate), samples behave satisfactorily up to 5.4 (28% toxicant) and up to sample 6.4 (14% toxicant) in series 6, according to Argentine standards.

In this way the importance of reinforcing toxics to improve the effectiveness of antifouling paints is clearly evidenced.

EXTENDER TYPE

In series 1, 2, 3 and 7, ferric oxide is used as extender. In series 4, 5, 6 and 8, calcium carbonate replaces ferric oxide with a consequent increase in the antifouling effectiveness, even in formulations with a high extender content such as samples 6.5, 6.4 and 8.4.

With the object of providing wider information on paint performance with both extenders, the influence of the extender type on the volume and specific diversity of the fouling community was analyzed.

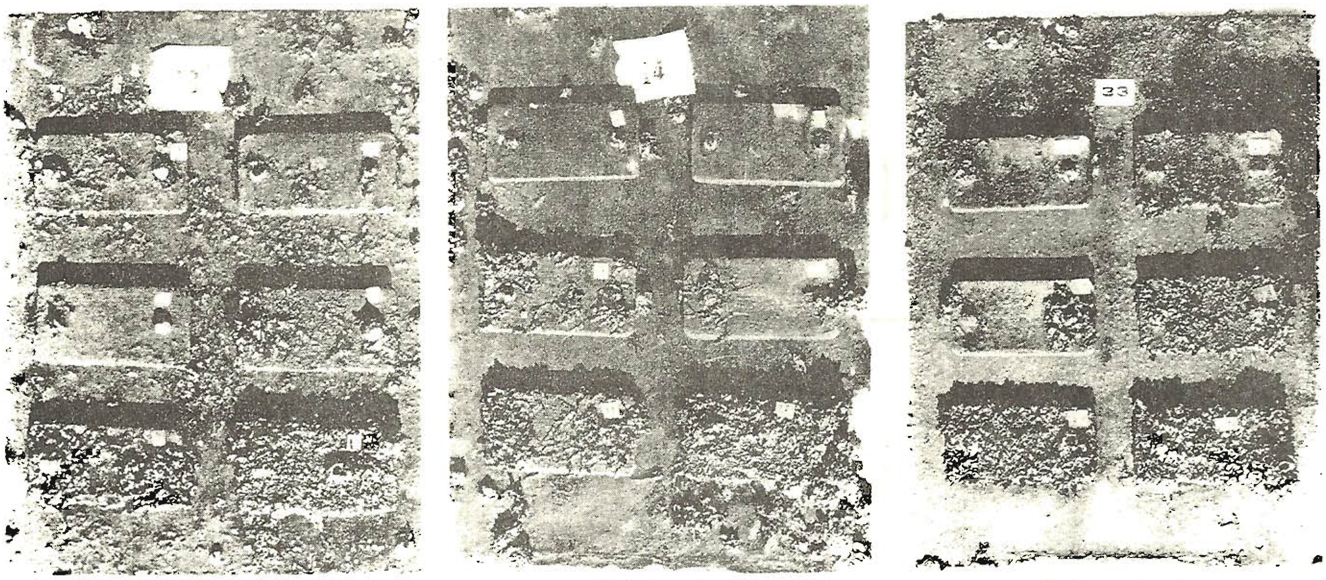
Figure 7 shows that in the complete series of paints as well as in the groups of series, calcium carbonate contributes qualitatively and quantitatively in the control of fouling settlement.

It is particulary significant that samples number 5 with a very low toxicant content (14% in the oleoresinous paints and 16% in the vinyl paints) still control fouling settlement after a twelve-month period. Mean fouling volume for these paints is 15.1 ml (with an extremely low value of 2.8 ml in sample 6.5) while in non-toxic reference plates, a fouling volume of 60.2 ml is observed.

FINAL CONSIDERATIONS

The present study has shown that tests on plates of minimum area prove quite advantageous for investigations on fouling communities and their adequate control. This method results in a better use of raft space facilities and the possibility of testing a higher number of samples simultaneously. On this occasion paints were tested on two different substrates (steel and acrylic plates) with the object of determining in which cases fouling attachment was due to failure on the antifouling paint or the corrosion phenomena, mainly in the edges of the plates.

On the basis of these results, it will be possible to apply statistical models in future research in this subject. On the other hand, this method will prove useful in the simultaneous study of a higher number of variables affecting the properties of antifouling paints.

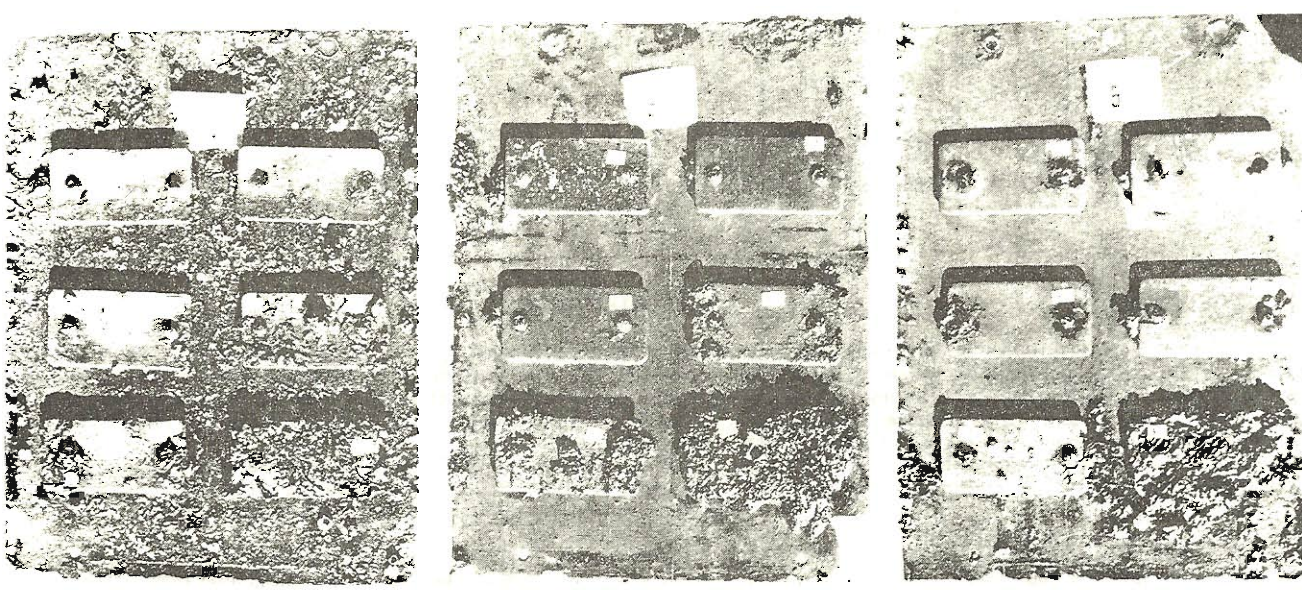


Paints series 1
Cu_2O-ZnO-Fe_2O_3
oleoresinous binder

Paints series 2
Cu_2O-ZnO-AsO_4Hg_3,
oleoresinous binder

Paints series 3
Cu_2O-ZnO-AsO_3Cu_3,
oleoresinous binder

Fig. 8
Aspect of the test plates after a 12 month exposure period in the experimental raft at Mar del Plata's harbour



Paints series 4
Cu_2O-ZnO-$CaCO_3$,
oleoresinous binder

Paints series 5
Cu_2O-ZnO-AsO_4Hg_3-$CaCO_3$,
oleoresinous binder

Paints series 6
Cu_2O-ZnO-AsO_3Cu_3-$CaCO_3$,
oleoresinous binder

Fig. 9
Aspect of the test plates after a 12 month exposure period in the experimental raft at Mar del Plata's harbour

From a biological point of view, the surface of the new plates seems appropiate for the recollection of fouling samples. This is specially true in the determination of attachment cycles of main species and in the study of the first stages of community development, and was corroborated by comparison with samples obtained from bigger plates (30 × 40 cm) such as those previously used.

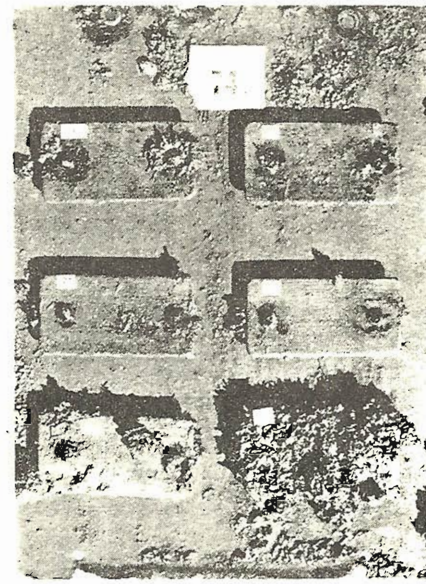
The study of the community over a one-year period has proved that progressive changes due to pollution in the harbour area are taking place. The abundant presence of *Polydora* seems to be a good biological indicator of pollution phenomena. On the other hand many fouling species which were common in previous years have disappeared from the area.

The fouling community can be considered as extremely aggressive, both for the high toxicant-resistance of its components as for its high rate of development. Fouling volume and specific diversity increase with time of immersion up to a stage of development in which dominant species become dettached from the plate. This moment marks the beginning of a new colonizing cycle (fig. 4, table VII).

Attachment and evolution graphs of main fouling species on long-term inert panels indicate certain differences in diatom behaviour (fig. 2 and 3). One group of diatoms colonize the plates rapidly and remain in low densities along the whole evolutionary process. This is the case of *Coscinodiscus*, *Licmophora* and *Synedra*. In other species, such as *Melosira*, *Nitzschia* and *Navicula*, the influence of seasonal attachment is clearly observed during the first three months of immersion; after this period their number decreases markedly.

Among animal components, some species join the community from the beginning of the assay and remain so till the end of the annual cycle (nematodes, *Polydora* and *Zoothamnium*). Other species make their appearance in a latter period (*Bugula*, *Bowerbankia* and *Ciona*) and compete with early settlers.

Paints series 7
Cu_2O-ZnO-AsO_4Hg_3-Fe_2O_3,
vinyl binder



Paints series 8
Cu_2O-ZnO-AsO_4Hg_3-$CaCO_3$,
vinyl binder

Fig. 10
Aspect of the test plates after a 12 month exposure period in the experimental raft at Mar del Plata's harbour

On the basis of fouling data (volume, wet weight, dry weight and specific diversity) obtained from inert and toxic plates, it was possible to devise a fouling settlement evaluation scale for antifouling paints based on a quantitative analysis. Indeed, all quantitative data are closely related with the degree of fouling attachment and complement paint evaluation methods with the scale from 0 to 5 previously employed (table IX). Simultaneous use of this information and direct observations as well as photographs of the plates, assures a very accurate qualification of the tested plates, based on biological evidence.

With regard to paint formulations, differences in bioactivity in each series are clearly observed (fig. 8, 9 and 10). In spite of close distances between panels, paints do not interfere with one another nor with the painted surface of the supporting panel.

Total toxic content of the paint film is an important factor affecting antifouling paint performance. However, the use of reinforcing toxicants, such as mercurous arsenate or cuprous arsenite, increases the toxic action as has been observed in series 2, 5 and 6 (fig. 6).

With the use of an adequate binder composition paint performance has been improved, even with low toxicant content. No settlement occurs on an oleoresinous sample with 14% toxicant by weight in the dry film (sample 6.5) after a year of immersion. This is also the case of a vinyl paint (sample 8.4) with 33% of toxicant (fig. 6).

Calcium carbonate used as extender has proved an effective complement in the bioactivity of the tested paints.

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