

CHAPTER 18

Characteristics of Antifouling Coatings

Although the qualities necessary for a successful antifouling coating are generally recognized and agreed upon, there is little agreement concerning the composition and formulation of antifouling coatings. In part, the disagreement has been the result of a failure to understand the mechanisms of antifouling action, and the resulting empirical and sometimes irrational approach to the problem. Some of the difficulty has arisen because preconceived ideas useful in other paint fields are of little or no value in formulating antifouling paints.

This chapter attempts to resolve some of these difficulties by restating the problem, defining the necessary terms, describing some satisfactory formulations, and summarizing the important properties of ingredients commonly used in antifouling paints.

GENERAL REQUIREMENTS OF ANTIFOULING COATINGS

Antifouling Properties

The ideal surface for prolonged protection would presumably be one which could act without consumption of the coating. To the best of our knowledge, no such paint has been designed. Any effect due to toxicity of the ingredients requires the gradual wasting of the paint because, to be effective, the poison must dissolve from the coating. The life of a toxic paint is determined by the thickness of the coating, its reserve store of toxics, and its rate of dissolution or wearing away. The mechanisms by which adequate toxic release may be obtained have been discussed in Chapter 16. The effective coatings appear to act by poisoning the organisms at the time of attachment or shortly thereafter.

Shipbottom paints prevent fouling for only a limited time. The aim of antifouling paint research should be to develop coatings which are effective for longer periods. The usual commercial paints in our experience have an average effectiveness of three to six months under subtropical fouling conditions. Very few are effective for periods as long as one year. The plastic type of antifouling paint developed by the Navy resists fouling for a much longer period, and has permitted the extension of the interdocking interval from six to eighteen months. Many ships coated with these paints

have been in operation in the Pacific for more than two years without fouling. As a result, the docking interval is now determined by the necessity for repairs to the hull and submerged fittings.

Durability

The durability of the coating depends upon its resistance to mechanical damage, the erosive effects of water movement, and the softening or solution of the components of the paint. Since the paint must disintegrate slowly to permit the liberation of the toxic, a compromise must be made between toxicity and durability.

Resistance to the erosive effects of water movement is a particular problem in connection with high speed vessels, such as motor torpedo boats and hydroplanes. It is probable that special paints which may sacrifice certain other properties to the development of a hard, tough surface will always be necessary for such craft.

The loss of durability of a paint film is generally most obvious at the water line. Mechanical damage resulting from floating debris or chafing on booms, and the repeated wetting and drying, combined with direct exposure to the sun, undoubtedly accelerate the breakdown of the paint system in this region. As yet no compositions have been designed for the water line area which give the service life attained by paints applied to the underwater sections of the hull.

Adhesion

The coating must adhere to the wood or steel of the ship's bottom. It is not sufficient that adhesion be satisfactory when the paint is applied under favorable circumstances. The coating should adhere well when applied under the far-from-ideal conditions of dampness and temperature under which much painting is done, particularly during winter in temperate latitudes. The frequently observed variations in the performance of the same paint on different occasions may be due largely to the variable conditions under which it is applied.

Effect on Corrosion

It is essential that the shipbottom paint system used on a steel vessel should protect the hull from corrosion. If the coatings do not prevent rusting,

the continuity of the paint will be destroyed and fouling of the bared areas will result. At least one coat of primer or anticorrosive paint is applied before the antifouling coating. The effectiveness of this anticorrosive paint may determine, to a large extent, the success of the antifouling material.

The antifouling paint may contribute materially to the protection of the hull from corrosion. This contribution depends primarily on the thickness of the coating and its resistance to the penetration of sea water. Experiments with the Navy paints show that the anticorrosive coating alone (about 2 mils) will prevent corrosion for only a few months. The addition of a coat of the cold plastic antifouling paint (about 5 mils) extends the protection to at least fifteen months, and the use of a thirty mil coat of the hot plastic antifouling paint will prevent serious corrosion for at least thirty months. Thick paint films thus aid in preventing corrosion, in addition to providing the necessary toxic reserve for prolonged prevention of fouling.

The ingredients of the antifouling paint should not accelerate the corrosion of steel. The common toxic pigments, metallic copper, and salts of copper and mercury, tend to accelerate corrosion if they are not adequately separated from the steel hull, as will be discussed in Chapter 22. For this reason it is very desirable that toxics other than these be developed for antifouling coatings.

Smoothness

The antifouling coating should have a smooth surface in order to keep the frictional resistance of the vessel to a minimum. The smoothness of the coating will depend upon the behavior of the paint film during drying.

Smoothness is a quality which acquires increased importance where speed is essential. Small racing yachts commonly employ paints which sacrifice much of their antifouling virtue for the sake of a hard, smooth finish. This may be done since it is easy to haul such craft for cleaning at frequent intervals.

The thick coatings which are required to provide prolonged protection against fouling must be carefully formulated to permit easy application, freedom from sagging, and good leveling. If drying is inadequate, a thick coating may tend to flow when the ship gets under way, and thus become rough (see Figure 13, Chapter 2). On the other hand, the viscous paints necessary to give thick coatings have sufficient body to fill up minor irregularities of the ship's surface.

Ease of Application

The antifouling paint should be designed to permit its application by either brush or spray equipment, so that vessels may be painted wherever it is convenient to dock them, and by whatever labor is available. The use of modern spray equipment results in great economies of time and in superior applications. Many commercial paints can be sprayed with standard equipment; the Navy has developed methods for spraying both the hot and cold plastic paints. Paints which can be applied by only one of these methods, such as the hot plastic which must be sprayed, are of necessity limited to those dry-docks using the appropriate method of application.

Wide variations in temperature should not seriously alter those properties of the paint which determine the ease of application, since vessels must be painted in all seasons and climates. Many formulations become undesirably thick in cold weather. The paint should be formulated so that readily available solvents are suitable for thinning. It should not cake in the container, or body excessively in storage.

Drying Time

Because the time available for painting is usually limited by practical considerations, it is essential that the paint dry rapidly. Commercial shipping firms generally restrict the docking periods to one day, part of which is required for cleaning the vessel. As a result, adequate painting is impossible unless the paints dry rapidly. If the time in dock is not too limited, multiple coats may be applied and thus provide the thick coating necessary for prolonged antifouling life.

If the paint film does not harden before the ship gets under way, the erosive action of the water may cause it to flow, thus impairing the serviceability of the coating. It has been found that many paints harden under water, so that a stationary period after undocking may aid in preventing excessive erosion or flow of the paint surface.

It has been traditional to float vessels as soon as possible after the application of the final antifouling coat. Tests on several proprietary paints which recommend this indicate that it either has no effect on the fouling resistance of the paint, or actually impairs it. It is probable that this recommendation is a carry-over from the days of the shellac paints, when water-soluble alcohol was used as the solvent. Its continuation is greatly favored by boat yard and dock owners who are anxious to keep their railways clear.

Color

Yachtsmen frequently choose the color of their bottom paints for esthetic reasons. Since the best toxic pigments are not of the desired colors, particularly the greens, many inferior yacht paints have been produced for this trade. Bottom paints used on work boats of all sorts are not usually especially colored. Submarines are frequently painted black for tactical reasons. The introduction of the tinting pigments commonly impairs the anti-fouling effectiveness of the paint. A similar problem is introduced in flying-boat hulls, where the need for a pale color has precluded the use of cuprous oxide, the toxic most approved in anti-fouling paints for ships.

Color has also been considered an important factor in determining the degree of fouling on submerged surfaces. This has been discussed in Chapter 13.

Expense and Availability

The cost of the paint normally constitutes only a small proportion of the total expense encountered in docking a vessel. An inefficient paint, no matter how cheap, does not represent a good investment. However, far too often price rather than performance is the dominant factor in the formulation and purchase of antifouling paints.

The following charges incurred by an 18,000-ton passenger liner, docked during 1940 in the San Francisco Bay area, show that the paint costs were less than one-third the total expense (10).

Dock Charges	\$1,800.00
Labor of Cleaning and Painting	1,300.00
Cost of Anticorrosive Paint	400.00
Cost of Antifouling Paint	750.00
Cost of Boottopping Paint	150.00
	<hr/>
	\$4,400.00

This ship is docked and repainted every nine months. It would be economical to pay at least double the quoted price for a more efficient anti-fouling paint if the docking interval could be extended by as little as three months.

For strategic reasons, the Navy uses domestic materials as much as possible in order to avoid the curtailment of supplies which might result during wartime. This consideration led the Navy to develop paints using rosin as the binder in place of the gum shellac employed prior to 1926. More recently it has been possible to make satisfactory antifouling paints which do not contain mercury as the toxic. The elimination of this material, which is both expensive and scarce, has saved

many thousands of dollars each year.

Many of the synthetic resins which are being developed are more expensive than the common natural resins. Their use may be restricted to paints intended for purposes which justify the extra expense. They may be added in small quantity to improve the qualities of paints which use cheaper materials as the main film-forming ingredient.

During wartime many materials which are normally available in adequate amounts may become scarce. It is frequently necessary under these conditions to modify formulations by the substitution of similar but more available materials. Since small changes in formulations may have a profound effect on the serviceability of the paint, it is essential to understand the properties of alternative ingredients so that substitutions may be made without detriment.

CLASSIFICATION OF ANTIFOULING PAINTS

Antifouling paints differ from other types of formulations because they must be designed to permit the release of the toxic. Two mechanisms which provide for this have been described. Paints made with matrices insoluble in sea water must contain a sufficiently high loading of the toxic to permit continuous contact of the toxic particles. Paints made with soluble matrices are effective with much lower loadings, since the dissolution of the matrix in sea water exposes stores of toxic from within the film. Permeability of the film has also been suggested as a mechanism to permit leaching of the toxic. The data available, however, indicate that the films, though permeable to water, are relatively impermeable to the toxic ions. So far as is known, no paints have been designed which are effective solely because of the permeability of the matrix (cf. Chapter 16).

Insoluble Matrix Paints

These paints require a high loading of the toxic pigment, and, consequently, a tough, durable binder must be used. The materials which have proved successful include the polyvinyl resins and short-oil length, water-resistant varnishes. It is probable that alkyd resins, chlorinated rubber, cellulose derivatives, and other high polymers could also be used. The resin may be the sole binder of the paint, or it may be plasticized or modified by the addition of other, less highly polymerized resins.

Metallic copper and cuprous oxide are the

toxics commonly used in these paints. Mercury compounds could presumably be used, but the cost would be excessive in view of the high loading required. A pigment volume loading of greater than 30 to 40 per cent cuprous oxide or 20 to 25 per cent metallic copper has been found necessary to insure continuous contact leaching (cf. Chapters 16, 19).

Examples of satisfactory formulations made with insoluble matrices are given below:

INSOLUBLE MATRIX PAINTS, HIGH POLYMER TYPE

		<i>Proportions by Weight</i>			
		<i>BK1</i>	<i>AF14</i>	<i>AF22</i>	<i>AF23</i>
Matrix	Vinyl resin	10	8	6	6
	Rosin		8	18	18
Pigment	Cuprous oxide	90	84	76	
	Metallic copper				76

INSOLUBLE MATRIX PAINTS, VARNISH TYPE

		<i>Proportions by Weight</i>		
		<i>80-4</i>	<i>6782</i>	<i>6803</i>
Matrix	Phenolic resin	9	6	6
	Cumar, hard		18	18
	Linseed oil	9	5	5
	Chinawood oil	9	5	5
Pigment	Cuprous oxide		50	
	Metallic copper	73		50
	Iron oxide		8	8
	China Clay		8	8

These paints are usually characterized by hard, erosion resistant films, and when correctly formulated have excellent long-term fouling resistance. They are expensive because of the necessary high loading with an expensive pigment. The high polymer paints are difficult to brush, and are best applied by spray. Unusual care in surface preparation is sometimes necessary for good performance and satisfactory adhesion. The varnish base paints are easily applied and have excellent adhesion, even on a poorly prepared surface. The continuous contact type metallic copper paints should not be used on steel vessels because of the danger of corrosive effects (cf. Chapter 22).

Soluble Matrix Paints

The matrix of these paints must contain a resinous ingredient sufficiently soluble in sea water to maintain adequate leaching of the toxic, but not so soluble as to result in the rapid deterioration of the film. Rosin is commonly used for this purpose, since its solubility appears to be within the limits required. Since rosin is brittle, it is generally plasticized to obtain flexibility. A large variety of plasticizers has been found satisfactory (cf. Chapter 19). High molecular weight resins, which may be added to toughen the film, reduce the rate of solution of the matrix, which tends to be excessive

when rosin is the principal film forming ingredient.

The plastic paints in use by the Navy have matrices soluble in sea water. The hot plastics are applied in the molten state and solidify on cooling. Two examples of hot melt paints formulated with a soluble matrix are given below:

SOLUBLE MATRIX PAINTS, HOT MELT TYPE

		<i>Proportions by Weight</i>	
		<i>42-3</i>	<i>19-92</i>
Matrix	Rosin	28	40
	Paraffin	36	24
Pigments	Cuprous oxide	36	28
	Magnesium silicate		8

The paraffin wax in these formulations acts as a plasticizer of the film and results in low viscosity of the melt, so that application is facilitated. The substitution of other waxes for the paraffin may improve the physical properties of the film, but generally decreases the rate of solution of the matrix with a resulting loss in fouling resistance.

The hot melt type paints are best applied by spray, and special equipment for this purpose has been designed by the Navy. Use of this equipment permits rapid application of a 20-50 mil pinhole-free paint film in a single coat. Such a film has been found to be effective in preventing fouling for periods of two to five years on naval vessels. Sufficient stores of toxics are present to provide an adequate leaching rate for at least ten years, though this limit has not been realized in practice. The rapid solidification of the film, which makes a prolonged period of drying unnecessary, is an advantage. The disadvantages include the relatively low coverage per gallon and the specialized heated spray equipment required for application. These paints are difficult to apply at air temperatures below 40°F, and the films have poor flexibility at low temperature.

Several examples of the solvent type antifouling paints with soluble matrices are given below:

SOLUBLE MATRIX PAINTS, SOLVENT TYPE

		<i>Proportions by Weight</i>			
		<i>15RC</i>	<i>105</i>	<i>16X</i>	<i>16XM</i>
Matrix	Rosin	27	29	26	26
	Navy 4B Resin				
	Pine oil	4			
	Coal tar	7			
	Coumarone-indene, soft		12		
	Zinc stearate		2		
	Tricresyl phosphate				
	Methyl abietate, hydrogenated			13	13
	Chlorinated rubber				2
Pigments	Cuprous oxide	15	27	52	51
	Mercuric oxide	5	4		
	Silica, amorphous	8			
	Zinc oxide	26			
	Magnesium silicate	8	6		
	Iron oxide, red		20		
	Silica, diatomaceous			9	8

This type of antifouling paint can be formulated to have a service life of well over a year. The paints can be inexpensive, simple to manufacture, and easy to apply, though they generally have relatively poor resistance to erosion by water. The poorer examples are extremely soft and unsuited for use on high speed vessels. The formulations given above vary widely in all of these characteristics. Formula 15RC, with its low toxic loading, prevents fouling for only a short time and is very soft. Formula 16X (30) resists the attachment of fouling organisms for more than a year when properly applied. The erosion resistance of 16X is not great, though it is better than 15RC. It is improved greatly by the addition of small amounts of chlorinated rubber, as in 16XM, or of various other long chain resins of large molecular weight which toughen the paint film (31, 36; cf. Chapter 19). The film properties of 105 are the best of these examples. Its resistance to fouling is erratic, however; some samples prevent fouling for long times, while others fail rapidly.

All of these paints may be applied by either brush or spray, and are suitable for application in cold climates where the hot melts fail. They form thinner coats than the hot melts, which limits their effective life. Since their impenetrability to water is not as great as that of hot melts of equivalent composition and thickness, they are not so effective in preventing corrosion, and their use requires an effective anticorrosive paint. They give good performance even when applied under adverse atmospheric conditions and with inadequate surface preparation.

INGREDIENTS COMMONLY USED IN ANTIFOULING PAINTS

The design of antifouling paints which operate by either the mechanism of continuous contact in an insoluble matrix, or by dissolution of a soluble matrix, requires specialized knowledge of the chemical and physical properties of the ingredients. In a book of this scope, it is impossible to include all ingredients which have been or might be used in antifouling paints. Gardner's lists of paint raw materials fill more than a hundred pages (19), and new synthetic resins and other products are constantly being produced. The purpose of this section is, therefore, to describe briefly the properties of some materials which make them useful in antifouling paints. For more extensive information on these and other possible ingredients, the standard treatises, such as those of Mattiello (27) or Ellis (17), should be used.

The ingredients used in formulating antifouling

paints generally perform the same function as in other types of coatings. Thus the matrix may contain a resinous ingredient which forms the continuous solid film. Plasticizers may be added to give a more flexible coating, and small amounts of long chain, large molecular sized compounds may be needed to increase the toughness and erosion resistance of the film. The peculiar property of some matrix ingredients which is important in antifouling paints is their solubility in sea water. This property is undesirable in other coatings, but is indispensable for the formulation of certain types of antifouling paints. The most useful soluble matrix ingredient is rosin, which is found in most of the satisfactory formulations.

It is apparent that different matrix ingredients are required in the two main types of antifouling paints: those with an insoluble, and those with a soluble matrix. Moreover, the same compound may be used for different purposes in these two types of formulations; the vinyl resins, for example, may be used in small amounts as tougheners of a paint with a soluble matrix, or may be the principal film forming ingredient of a paint with an insoluble matrix (31, 41).

The pigmentation of antifouling paints is readily divided into toxic and nontoxic pigments. The toxic pigment must have a small but finite solubility in sea water in order to be effective. If the toxic is too soluble, it may be extracted rapidly and completely from the film. If, on the other hand, it is too insoluble, it will not dissolve sufficiently to prevent fouling (cf. Chapter 14, 15). Thus, cuprous oxide or metallic copper have satisfactory solubilities, but cupric oxide is too insoluble to be effective, and several copper compounds such as the sulfates and chlorides are too soluble. Mercuric oxide and mercurous chloride are satisfactory mercury compounds but mercuric chloride is too soluble for effective use.

Nontoxic pigments may be added to obtain a suitable volume loading for the vehicle, to aid in suspending the heavier pigments and avoid caking in the can, or, with proper attention to particle size and shape, to increase the toughness of the paint (11, 18). The addition of small quantities of nontoxic pigments to paints containing moderate or low amounts of the toxic pigment has been reported to improve the antifouling properties of the paint.

Matrix Ingredients

Natural resins: One of the commonest ingredients of antifouling paints is rosin which is obtained from pine trees. The value of rosin as an antifouling

paint component was established by empirical formulation. Its function as a soluble matrix ingredient has only recently been recognized (cf. Chapters 16, 17).

Commercial rosin is classified by color, which is largely determined by the amount and types of impurities present.¹ In the highly pigmented antifouling paints, the color of the rosin used is of little importance, though the lighter grades are often specified. Actual tests show that all grades of gum rosin and all grades of wood rosin except FF and B have suitable solubilities.

There are many other natural resins, differing widely in properties, which have been tried in antifouling paints. None of them is more satisfactory than rosin, though shellac has been extensively used. Since the latter is imported from India, its use was discontinued in 1926 by the United States Navy in favor of domestic materials. Yacca gum was introduced by Adamson as a partial substitute for gum shellac (2). This material is less acid than rosin, and consequently less soluble in sea water.

Treated natural resins: The properties of the treated natural resins vary widely, and some are available which are useful in each category of paint ingredients (i.e., resin, plasticizer, toughener). Many of the treated resins are neutral and therefore insoluble in sea water.

Ester gum, the glyceryl tri-ester of rosin, is nearly neutral and insoluble in sea water. Its substitution for all of the rosin of an effective antifouling formulation generally makes the paint unsatisfactory, since it excludes the water from the toxic materials. Its use in smaller quantities may improve the performance of the coating by stopping the excessive wasting which occurs in paints containing large amounts of rosin.

The rosin salts of divalent cations form the so-called hardened rosins, which are practically insoluble in sea water. Copper resinate has been suggested frequently for use in antifouling paints (15, 17, 26, 28, 37). The negligible solubility in sea water makes it of little value as a toxic agent, but in some formulations it is useful as a plasticizer. Copper resinate is formed in all paints containing both rosin and copper compounds. This reaction renders insoluble a portion of both the matrix and the toxic. If formed in too great quantities, the antifouling properties of the paint may be destroyed.

The hydrogenated rosin esters, such as hydrogenated methyl or ethyl abietate, give liquid resins which have been useful as plasticizers in antifouling paint films.

Modified rubber resins, such as chlorinated and cyclicized rubber (17, 38), have been found useful as toughening agents for antifouling paints. Chlorinated synthetic rubber has also been used successfully (29). They are generally added in very small proportions (less than 5 per cent of the dry film), but some paints have been made in which the modified rubber is a large part of the binder. Modified rubber films are extremely resistant to both acid and alkali, and are completely insoluble in the slightly alkaline sea water.

Synthetic resins: A great variety of synthetic resins is available, but only a few have been used in antifouling paints. It is probable that many more are now being tested in various industrial laboratories.

The alkyd resins are reaction products of polyhydric alcohols (glycol, glycerol, etc.) with polybasic acids (chiefly phthalic, also maleic, succinic, etc.). The alkyds used in the paint industry are generally modified with the fatty acids obtained from linseed or soy-bean oils. This improves their solubility in the common paint solvents, and the product gains some of the properties of the oil employed.

Alkyd resins have been used extensively in preparing paint coatings. In the underwater paint field, their use has been largely restricted to the anticorrosives and primers. They have not been used as the binder of continuous contact paints. Their inclusion in the proper proportions in rosin base, soluble matrix type paints may give desirable film characteristics.

The coumarone resins are reaction products of coumarone and indene. They are completely neutral and insoluble in sea water. Five different grades are recognized, ranging in melting point from 5° to 160°C (17, 22). The softer grades have been used as plasticizers in antifouling paints, and the harder grades have been mixed with rosin or with drying oils to form the binder.

Phenolic resins, modified with rosin, have been used in hot melts and solvent type antifouling paints. Frequently, phenol and formaldehyde, together with lead acetate as a catalyst, are reacted in the presence of rosin during the varnish cook. The resin obtained is less soluble in sea water than rosin alone. The use of rosin esters in place of the rosin, though common in the manufacture of varnishes where water resistance is desirable, is generally not satisfactory for antifouling coatings.

¹ These are in order of increasing color X, WW, WG, N, M, K, I, H, G, F, E, D, B. Twelve color standards have been developed by the Naval Stores industry. The primary standards for comparison are 1/8 inch glass cubes adapted by the Bureau of Chemistry and Soils, U. S. Department of Agriculture (24, 35).

Phenolic resin-drying oil varnishes have been used to formulate paints of the continuous contact type, where insoluble, tough matrices are desirable.

The vinyl resins which have proved useful in antifouling formulations include the vinyl chloride-acetate copolymer and polyvinyl butyral. These resins are extremely tough and resistant to solution by sea water. They have been used as the sole binder in antifouling paints, and require an extremely heavy loading of the toxic pigment to provide the continuous contact necessary to maintain an adequate leaching rate. Vinyl resins have also been used with considerable success to toughen paint films which contain rosin as the principal binder.

The polyvinyl butyral resins may form a gel in an antifouling paint on storage. This gelation appears to result from the reaction of residual hydroxyl groups of the resin with the heavy metal toxics. Frequently, the antifouling action of the paint is impaired before the gelation becomes apparent.

Cellulose products have been useful as toughening and modifying agents for various types of antifouling paint films. Ethyl- and benzylcellulose have both been used to toughen paint films containing large amounts of plasticized rosin as the binder. Nitrocellulose lacquers have found very little application in antifouling paints, though they may be used at times to provide a hard, smooth finish for small racing yachts where antifouling properties are not of great importance.

Drying oils: Chinawood, dehydrated castor, tung, and linseed oils are used in short-to-medium oil length varnish vehicles to formulate paints with an insoluble matrix. Bodied linseed, chinawood, and fish oils have been used to plasticize rosin-containing antifouling paints. Unmodified drying oil coatings do not give good performance on underwater exposure.

Tar products: Tar, pitch, bitumens, creosote, and other products of the destructive distillation of wood and coal are common ingredients of bottom paints. Toxic properties have been attributed to these products, though they alone will not prevent fouling for very long (32). They may have some virtue as wood preservatives, and they do protect wooden structures from the depredations of the wood destroyers, *Teredo* and *Limnoria*.

Pigments

The primary purpose of the pigment in antifouling paints is to provide the toxicity necessary to prevent the attachment of fouling. The pigments also give body to the paint, and harden

and strengthen the coating. Although many effective paints contain only the toxic pigments, various nontoxic or inert pigments have been used to improve physical durability, application characteristics, or appearance. The nontoxic pigments are cheaper than the toxic pigments, and are frequently employed in undesirably large amounts.

TOXIC PIGMENTS

A great many pigments have been included in antifouling paints to provide toxicity, though very few have stood the test of use. Table 1 in Chapter 14 shows the toxicity of solutions of various compounds of heavy metals to marine organisms, and may be used to judge the usefulness of these compounds in paints. The most commonly used toxics are compounds of copper, mercury, and arsenic. All of the British proprietary antifouling paints studied by Bengough and Shephard (7) contained both copper and mercury. In addition 67 per cent of the paints tested contained arsenic compounds.

Cox (12, 13) has reported the toxic constituents of 46 proprietary American antifouling paints submitted for test and sale in California, including bronze, red and green compositions. Copper or copper compounds were present in all but one of these in amounts ranging from 0.44 to 29.5 per cent (expressed as metallic copper). Mercury was present in seventeen in amounts of 0.39 to 15.8 per cent. Arsenic in amounts of 0.82 to 12.96 per cent was present in 15 paints. Eight of the paints contained all three toxics, and 22 contained only the copper. After six months' exposure in southern California waters, the performance of these paints varied from excellent to valueless.

It is apparent that there is little or no agreement among manufacturers as to the amount or type of toxics to be employed. The fact that more than 40 per cent of the paints tested in California were not acceptable shows that considerable improvement in proprietary formulations is possible.

The American Society for Testing Materials issued specifications for the toxic content of antifouling paints (5). The cuprous oxide specified must all be present in the reduced form, any cupric oxide being considered as inert material. Their specifications were as follows:

	General Service	North Temperate Waters	South Temperate Waters	Tropical Waters
Cuprous oxide, oz. per U. S. Gal., not less than	14	25	20	14
Mercuric oxide, oz. per U. S. Gal., not less than	7	1.5	5	14

These specifications require that both copper and mercury be used as toxics in antifouling paints, and do not take into account the matrix constituents, which are at least as important as the toxic. It is also probable that the toxic content of the dried paint film is more important than the content per gallon, since different spreading rates can be obtained by manipulating the vehicle and solvents. Recent investigations indicate that these required amounts are too low. Young and Schneider (43) have found that metallic copper or cuprous oxide loadings of 6 lb./gal. were necessary in insoluble oil varnish vehicles.

Copper pigments: Several types of copper pigments have been used, and the success of paints made with them is largely dependent upon their solubility in sea water (cf. Chapter 15). Pigments with little or no solubility, such as cupric oxide, do not dissolve sufficiently to provide the necessary toxicity. Those which are too soluble, such as copper sulfate or chloride, may dissolve out of the paint film too rapidly, thus exhausting the film of its store of toxics, leading to rapid failure.

Cuprous oxide is a very effective toxic and is present in the common red copper bottom paints. It is used as the only pigment in some effective formulations. Since it can be obtained in very small particle sizes, it also acts as an effective bodying agent. Light, inert pigments, such as magnesium silicate and diatomaceous silica, are frequently added to the paint to avoid the caking of cuprous oxide on storage.

Metallic copper flake or powder is used in the commercial "bronze" paints. Since this material is very reactive with some vehicles, it is often packaged separately in two-compartment cans, to be mixed immediately before application. Metallic copper may be used in paste form to facilitate mixing. When applied over steel, effective primers must be used to avoid excessive corrosion. Tuwiner and Dodge (39) report the effective use of a metallic copper paint on a steel ship.

Basic copper carbonate has been tried in antifouling paints, but its composition is so variable that reproducible coatings are difficult to obtain. Practically the only recommendation for this pigment is that it is green, and can, therefore, be used in green bottom paints so much in demand by yachtsmen. Copper thiocyanate, sometimes called white copper, has been tried because of its adaptability to colored paints, but has been found less effective than cuprous oxide or metallic copper.

Paris green might be expected to be very effective because it contains both copper and arsenic.

Wehmhoff, Jordan, and Knight found it satisfactory in a hot plastic formulation (40). Adamson states that it requires fortification with copper or mercury salts in order to prevent fouling (1). Harris attributes its action entirely to the copper which it contains, and rates it as much less effective than metallic copper or cuprous oxide (20).

Young and Schneider (43) tested other copper-containing compounds, including the arsenite, oxychloride, oleate, linoleate, naphthenate, pentachlorophenate, and tetrachlorophenate, in two different vehicles. None of these was as effective as copper or cuprous oxide. They concluded that only compounds capable of releasing copper ions have utility as antifouling agents.

Mercury pigments: On the basis of the minimum leaching rate determinations, mercury is about five times as effective, weight for weight, in antifouling paints as copper (cf. Chapter 14). In certain formulations, however, it has been found to be only two to three times as effective as copper in preventing fouling (20). Since mercury pigments are almost ten times as expensive as the common copper compounds, even these advantages are inadequate to make the use of mercury economical. Mercury compounds are valuable in producing the lighter colored paints necessary for aircraft and prized by yachtsmen.

Mercuric oxide is quite soluble in sea water, and is very effective in maintaining an adequate leaching rate and in preventing fouling. Mercurous chloride is less soluble and has not been used so frequently, but has been successfully employed in antifouling paints for flying-boat hulls (4, 28). Mercuric chloride has an enormous solubility in sea water, and films made with this material tend to become exhausted rapidly.

Organic mercurial compounds have received some attention and offer some promise as effective antifouling agents (42). Their solutions are slightly more toxic than those of inorganic mercury compounds (33). The increased expense of these organic mercurial compounds is, however, reported to more than offset any advantage they might have.

Arsenic compounds: Arsenic has been detected in 67 per cent of a group of British proprietary paints (7, 20) and in 33 per cent of a group of American proprietary paints (12, 13). Several controlled experiments suggest that it has little or no effectiveness as an antifouling agent. Bray showed that Paris green, copper arsenite, arsenic pentasulfide, and diphenyl arsenious oxide were not very toxic to barnacle nauplii. Arsenic mixed

in a paint appeared to have no special value (8, 9, 16). Adamson (1) states that arsenic trioxide and arsenic trisulfide were not effective, the former probably because of its high solubility. In the same tests, Paris green required supplementing with mercuric oxide in order to prevent fouling. Harris found that arsenic was ineffective in preventing barnacle fouling (20).

Organic toxics: Organic toxics have several possible advantages over the heavy metal compounds generally used. They do not have the corrosion stimulating action of the metallic salts, and their use would be of strategic value, since they may be synthesized from commonly available materials. Many of them are specific in their toxic action, rather than general poisons such as copper and mercury. It would probably be necessary to reformulate the coating completely to use them effectively.

The toxicities of almost a hundred organic poisons are recorded in Table 12, Chapter 14. To give satisfactory antifouling performance, the material must be toxic to marine organisms, and only slightly soluble in naphtha. When added to normal paints, which depend on copper for the toxic action, an organic poison may affect the paint medium, may change the copper leaching rate, and may even result in decreasing the antifouling effectiveness of such paints. The use of organic toxics in cementiferous coatings appears to offer some promise (21).

The insecticide, DDT, has been found effective in preventing the attachment of barnacles, though it is not active against other fouling forms such as the bryozoans, algae, and molluscs (14, 25, 34). This is an example of the specific action of an organic toxic which makes it unsuitable unless fortified with more general poisons.

NONTOXIC PIGMENTS

Addition of pigments which do not have a demonstrable toxic action may contribute to the effectiveness of the coating. Young, Schneider, and Seagren (44) concluded that the addition of barytes to copper powder paints improved their antifouling performance. If the volume of toxic pigment required to give adequate protection against fouling is less than the total volume necessary for optimum film properties, nontoxic pigments may be added to obtain the proper pigment volume (cf. Chapter 19).

It has been found that antifouling paint formulations can be extended with a variety of nontoxic pigments without impairing their effectiveness

(3, 23). For each formulation, a critical concentration of toxic pigment must be maintained. The type of nontoxic pigment appears to be important in some formulations (3, 6, 23). Alexander and Benemelis (3) found that zinc oxide gave the most consistently satisfactory result in their vehicles, though they were able to produce equally good paints with a variety of toxic and nontoxic pigments.

Adamson (2) lists zinc oxide, zinc dust, iron oxides, silica, and magnesium silicate as the most commonly used nontoxic pigments in shipbottom paints. The zinc compounds are more frequently a part of the anticorrosive, but may also be used in the antifouling coatings. In addition to these, pigments such as chrome green, chrome yellow, and various lakes may be used for coloring purposes.

The investigators of the British Iron and Steel Institute reported the analysis of 47 proprietary paints which included both anticorrosive and antifouling shipbottom compositions (7). The following list shows the most commonly used pigments in these paints, and the proportion of the paints containing each pigment. Red iron oxide and zinc oxide were used most frequently and were major constituents of most of the paints tested.

<i>Non Toxic Pigments*</i>	<i>Frequency %</i>
Red Iron Oxide	23
Red Iron Oxide plus whiting or barytes	6
Red Iron Oxide and ZnO	23
Zinc Oxide, ZnS and barytes	19
ZnO alone or with barytes	9
Aluminum powder	4
Miscellaneous mixtures (Zn dust, red or white lead, calcium sulfate or phosphate and various combinations)	13
None other than toxic pigments	4

* List from reference 7, after J. C. Hudson.

The quantity of the pigments in antifouling paints varies widely. No controlled experiments have been reported on the optimum pigment loading for underwater exposures, and investigations in this direction would be valuable. The quantity of the toxic necessary for antifouling performance should first be determined by fouling tests or leaching rate experiments. The quantity of nontoxic pigments needed to give any particular total pigment volume may then be added. Many proprietary paints are unsatisfactory because they contain too little toxic, undoubtedly because the common extender pigments, such as the iron oxides, are much cheaper than the toxic pigments. The cost in 1944 of some of the toxic and nontoxic pigments is given as follows:

Toxic Pigments	Cost/lb.	Non Toxic Pigments	Cost/lb.
Cuprous oxide, electrolytic	\$0.240	Magnesium silicate	\$0.010
Cuprous oxide, pyrochemical	0.220	Silica, Amorphous	0.014
Copper flake	0.400	Silica, Diatomaceous	0.030
Mercuric oxide	2.00	Zinc oxide	0.075
		Indian Red	0.078
		Lamp Black	0.10

It is, therefore, economical to use as large a proportion of nontoxic pigments as possible to obtain the best physical properties of the paint. The toxic pigment must, however, not be reduced below the amount necessary for antifouling action. The interrelationship of these factors is discussed in the next chapter.

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