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CHAPTER 19

The Design of Antifouling Paints

The properties requisite for satisfactory performance of antifouling paints include durability, adhesion, smoothness, and ease of application as well as the ability to prevent the attachment or growth of fouling organisms. This chapter will attempt to define, insofar as is possible, how paints may be designed to have these desirable qualities. In many cases the influence of the paint ingredients on the properties of the film is not fully understood, and the design of improved formulations is thereby handicapped.

It must be emphasized that both the physical quality of the paint film and the antifouling properties are essential for the best performance. In the present state of the art, paints can be designed which do not foul so long as the physical integrity of the paint film is maintained. Further advances in the development of such paints will result from improvement in strength, toughness, and adhesion. The effects of paint ingredients on the antifouling properties are currently more clearly understood than are their effects on physical properties. Consequently, this chapter may appear to give undue emphasis to the toxicity of the paint. Since, however, paints may now be designed with the appropriate toxicity, it seems probable that rapid improvement in the knowledge and understanding of the effects of ingredients on the physical properties will be forthcoming.

Most, if not all, of the effective antifouling paints act because of one or the other of two mechanisms which have been described in Chapter 16. One group of paints, characterized by a high loading of toxic pigment and a tough, impermeable, insoluble matrix, maintains an adequate leaching rate because the toxic particles are in continuous contact throughout the dried paint film. The other group, characterized by lower loadings of the toxic pigment and the presence of rosin or another soluble ingredient in the matrix, maintains a satisfactory leaching rate because the matrix dissolves away, uncovering the stores of toxic within the film. The principles in the design of these two types of paint are entirely different and will be discussed in turn.

PAINTS WITH INSOLUBLE MATRICES

To give satisfactory performance, paints with insoluble matrices must contain the maximum loading of toxic consistent with the mechanical integrity of the paint film. The greater the loading of toxic, the more perfect the contact between particles and the longer the life of the paint. These high loadings, however, lead to a waste of toxic because of excessively high copper leaching rates during the early stages of immersion. As extraction proceeds, only that toxic which lies in chains of particles in contact and extending originally from the surface inward can be dissolved. The chance that a given particle is in such a chain decreases progressively with its distance from the surface. As the chains of particles dissolve away, a depth is ultimately reached where the continued solution of toxic is at an inadequate rate to prevent fouling. It follows that, for each such paint, a critical thickness may be determined beyond which adequate leaching will not continue. It is consequently impossible to extend the life of continuous contact paints by increasing the thickness of the film beyond this critical depth.

The Vehicle

The strength and integrity of the paint depend upon the resinous ingredients of the vehicle. Paints containing polyvinyl resins and high loadings of toxic have been developed by investigators at the Bakelite Corporation (*2*) and short-to-medium oil length varnish vehicles have been used by Young and his collaborators (*10, 11*). Probably many other high molecular weight synthetic resins would also be successful.

In paints using the vinyl resins it is unnecessary to use other resinous ingredients. Tougheners are not required, since the principal resinous ingredient itself is tough; plasticizers for this type of matrix have not been extensively studied. The use of rosin with polyvinyl resins increases the leaching rates by considerable amounts, and generally extends, by a month or more, the period during which adequate rates are maintained. It is possible that the solubility of the rosin contributes to the availability of the toxic. Rosin may be substituted for as much as 75 per cent of the polyvinyl resins in the matrix without decreasing the durability of the paint appreciably.

Pigmentation

Toxic loading: In developing a paint with an insoluble matrix, the first experiment required is one

TABLE 1. The Copper Leaching Rates of Vinyl and Vinyl-rosin Paints Containing Various Amounts of Cuprous Oxide After Various Periods of Immersion in the Sea

Matrix*	Toxic Wt. %	Toxic Vol. %	Leaching Rates (μg./cm.²/day) after: 0 mo.	1 mo.	2 mos.	3 mos.	4 mos.	5 mos.	6 mos.
A	90	65	146	64	61	29	20	14	9
A	80	45	92	41	39	23	17	11	8
A	70	33	79	16	16	9	7	5	3
A	60	24	23	0	2	1	—	—	—
A	40	12	12	1	2	1	—	—	—
B	90	65	161	97	104	39	17	14	12
B	80	45	135	68	72	40	13	8	4
B	70	33	111	54	45	26	14	9	5
B	60	24	37	8	3	4	—	3	2
B	40	12	42	1	1	1	—	—	—

* Matrix A contained only vinyl acetate-vinyl chloride copolymer resin; matrix B contained equal proportions of vinyl resin and WW rosin.

to determine the pigment loading necessary to give continuous contact of toxic particles so that an adequate leaching rate will be obtained (*3*, *4*).

Such an experiment using a vinyl resin matrix is shown in Table 1. The paints which contained less than 33 per cent cuprous oxide by volume gave leaching rates which dropped to very low values during the first month of immersion in the sea; the leaching rates of the remainder were adequate for progressively longer times as the loading with the toxic increased. The paints containing rosin in the matrix (B) have higher leaching rates and their effective lives are longer by a month or more than those of the paints containing only vinyl resin.

Similar experiments have indicated that a somewhat greater loading of cuprous oxide, 40 per cent by volume, is essential to give adequate copper leaching rates from a short-oil varnish vehicle. If metallic copper is used as the toxic, the loading must exceed only 20 per cent by volume (*49*). The difference in the critical value for the two types of toxic is probably related to the different shapes of the toxic particles. It is commonly believed that the leaf-like metallic pigments are arranged flat and parallel to the painted surface. Such an arrangement would require a higher loading for continuous contact than close packing of spheres. Lower loadings, however, have been found to give adequate results. Some degree of haphazard arrangement is necessary to produce the observed effect, and the pattern may be visualized as a "house of cards." This would give continuous contact at the edges of the particles, with relatively large spaces in between to be occupied by the matrix.

The effect of varying the loading of cuprous oxide and of metallic copper on the leaching rates of varnish type paints is shown in Table 2. The leaching rates of the paints containing less than 40 per cent cuprous oxide or 20 per cent metallic copper (by volume) fall during the first month to low and inadequate values. As the loading is increased, the leaching rates are maintained at higher levels for longer periods of time.

Nontoxic pigments: The presence of nontoxic pigments, in addition to the toxic, has been stated

TABLE 2. The Copper Leaching Rates of Varnish Vehicle Paints Containing Various Amounts of Cuprous Oxide and Metallic Copper After Various Periods of Immersion in the Sea

	Toxic	Toxic Wt. %	Toxic Vol. %	Copper Leaching Rates μg./cm.²/day after: 0 mo.	1 mo.	2 mos.	3 mos.	4 mos.
1	Cu_2O	85	50	41	25	20	22	
2		82	45	36	18	15	14	
3		79	40	20	10	8	9	
4		75.2	35	39	5[f]	4[f]	7[f]	4[f]
5		70.5	30	32	3[f]	3[f]	5[f]	3[f]
6		65.0	25	30	2[f]	3[f]	4[f]	2[f]
7		58.5	20	29	2[f]	2[f]	3[f]	2[f]
8		50	15	22	2[f]	2[f]	3[f]	1[f]
1	Cu	80	35	215	30	23	37	22
2		76	30	226	27	22	37	20
3		71	25	229	25	17	31	14
4		65	20	205	15	13	22	12
5		57	15	193	4[f]	6[f]	10[f]	8[f]
6		49	11.5	175	3[f]	3[f]	7[f]	4[f]

[f] Paint fouled at this time when exposed at Miami Beach, Fla.

to improve the performance of heavily loaded paints in a varnish vehicle (*11*). Since most paints contain nontoxic pigments, the investigation of their effect on the performance of the formulation is essential. The effect of the substitution of inerts in this type of formulation has been discussed in Chapter 16, where it was shown that the substitution of an inert pigment for an equal weight of matrix may result in an increase in volume fraction of the toxic pigment. This produces a greater probability of continuous contact between the toxic

TABLE 3. The Copper Leaching Rates of Vinyl Resin Paints Containing Diatomaceous Silica After Various Periods of Immersion in the Sea. The Leaching Rates of Paints Containing Comparable Amounts of Cuprous Oxide but No Silica, Are Given in Table 1

Paint Composition: Vinyl Resin wt. %	Cu_2O wt. %	Silica wt. %	Cu_2O Vol. %	Copper Leaching Rate μg./cm.²/day after: 0 mo.	1 mo.	2 mos.	3 mos.	4 mos.	5 mos.	6 mos.
15	70	15	40	108	21	33	17	10	8	5
20	60	20	30	83	13	16	10	6	5	3
25	50	25	22	82	11	7	6	3	2	2

particles, and results in a paint giving a higher leaching rate (*4*).

The substitution of diatomaceous silica for an equal weight of matrix in vinyl resin paints results in an increase in the copper leaching rate and in the effectiveness of the formulation. The compositions and leaching rates of several vinyl resin paints which contain various amounts of diatomaceous silica are given in Table 3. The comparison of the leaching rates of these paints with those in Table 1 containing an equivalent weight per cent of cuprous oxide, show that a considerable improvement in the performance of the paint has resulted. Comparison of the volume composition of these paints, however, indicates that the formulations containing diatomaceous silica give approximately the same leaching rates as those without the silica but with the same volume of cuprous oxide. The average copper leaching rates of these paints are plotted in Figure 11 of Chapter 16 against the volume fraction of cuprous oxide. This figure shows that the leaching rates of the paints appear to be related solely to the volume fraction of toxic, and

TABLE 4. Effect of Nontoxic Pigments on the Copper Leaching Rates of Varnish Type Paints Containing 15% Toxic by Volume

Weight Composition				*Leaching Rates μg./cm.²/day after:*				
Toxic	*Varnish Solids* %	*Inert* %	*Toxic* %	0 *mo.*	1 *mo.*	2 *mos.*	3 *mos.*	4 *mos.*
Cu_2O	50	0	50	22	2	1	3	1
Cu_2O	30	31	39	31	2	2	3	1
Cu	42.5	0	57.5	175	3	3	7	4
Cu	26	27	47	192	10	5	8	5

that the presence of the silica has no additional effect.

Within limits an inert pigment may be used effectively to improve the leaching of the toxic from antifouling paints. Most of the effect may be attributed to the increase in the relative volume occupied by the toxic when the inert pigment is substituted for an equal weight of matrix.

To determine the effect of inert pigments on leaching rates and fouling resistance at constant toxic loading, an experiment was performed in the varnish vehicle described above. Inert pigments were added in graded amounts to paints containing both 15 and 30 per cent of toxic by volume. Both cuprous oxide and metallic copper were used. Table 4 shows the results obtained at a toxic volume of 15 per cent, and Table 5 shows those at a toxic volume of 30 per cent. The weight fraction of the toxic decreases as the inert pigment is added. There is, however, essentially no difference

TABLE 5. Effect of Nontoxic Pigments on the Copper Leaching Rates of Varnish Type Paints Containing 30% Toxic by Volume

Weight Composition				*Leaching Rates μg./cm.²/day after:*				
Toxic	*Varnish Solids* %	*Inert* %	*Toxic* %	0 *mo.*	1 *mo.*	2 *mos.*	3 *mos.*	4 *mos.*
Cu_2O	30	0	70	32	3[f]	3[f]	5[f]	3[f]
	26	6.6	67.4	44	3[f]	2[f]	5[f]	3[f]
	23	12.7	64.3	40	4[f]	3[f]	5[f]	3[f]
	20	18.3	61.7	50	5	4[f]	8[f]	4[f]
	18	23.3	58.7	59	5	5[f]	8[f]	5[f]
Cu	23	0	77	226	27	22	37	20
	21	5	74	218	44	19	37	16
	18	10	72	200	24	20	28	15
	16	15	69	235	27	23	19	19
	14	19	67	242	25	24	18	16

[f] Paint fouled at this time when exposed at Miami Beach, Florida.

in the leaching rates or fouling resistance of these paints at either loading or with either toxic. This result confirms the conclusion that the major effect of inerts is associated with the change in the *volume* occupied by the toxic pigment.

In designing a paint of the continuous contact type two conditions must be met to obtain the best and most economical formulation: (*1*) the toxic volume necessary to insure adequate fouling resistance for the desired time, and (2) the optimum total pigment volume to give the best physical performance.

Any number of formulations can be made containing a given volume of the toxic pigment by varying the total pigment. For example, four formulations containing 35 per cent cuprous oxide by volume, whose total pigment volumes vary from 35 to 70 per cent, are given in Table 6. All of these paints should give approximately equivalent leaching rates and fouling resistance, but the physical performance of the paint films and the storage qualities of the paints would probably vary considerably because of the difference in pigment loading. The presence of the lighter inert pigment avoids, to some extent, the tendency of paints with high loadings of toxic to settle and cake excessively on storage.

If tests on physical performance showed the optimum pigment volume for the vehicle to be 60 per cent, this could be obtained by the addition

TABLE 6. Table of Paint Compositions which Contain 35% by Volume Cu_2O and Various Amounts of Nontoxic Pigments. The Following Bulking Values are Used in These Calculations:

Cu_2O = .0207; Vehicle = 0.1; Nontoxic Pigment = 0.05 gal./lb.

Cu_2O % by weight	72	68	65	63
Vehicle % by weight	28	20	16	11
Inert % by weight	0	12	19	26
Cu_2O Volume %	35	35	35	35
Total Pigment Volume %	35	50	60	70

of inerts, as in Table 6. If, however, longer antifouling life for the paint were desirable, the toxic pigment volume itself could be increased to 60 per cent (88 per cent Cu_2O by weight in the above example). Any intermediate combination of toxic and inert pigment could, of course, also be used, and would result in intermediate properties of the paint.

Should the optimum pigment volume for the vehicle turn out to be less than the volume of toxic required for satisfactory antifouling performance, the vehicle is not suitable for paints of the continuous contact type, and will not give the required performance with any combination of ingredients.

PAINTS WITH SOLUBLE MATRICES

If both the matrix and the toxic of a paint are soluble in sea water they will dissolve simultaneously. As the toxic in the surface layer dissolves away, the matrix also dissolves and exposes new and underlying layers of toxic. A paint of this sort can be effective with much lower loadings than the insoluble matrix paints, and, furthermore, if properly designed, will retain its toxicity until the entire paint film has been dissolved. It follows that an increase in the thickness of such a paint film will result in extending the antifouling life. The leaching rate may be controlled by varying both the toxic loading and the solution rate of the matrix, which permits greater latitude in developing the formulation (*5*). The matrix materials which have suitable rates of solution generally do not have the best physical characteristics and, consequently, the paints must be plasticized and sometimes toughened with resins of high molecular weight in order to give the most satisfactory service.

In the design of paints with soluble matrices, both the loading with toxic pigment and the composition and solution rate of the matrix must be considered. It is the solution rate of the matrix which determines the rate at which the toxic particles are exposed to sea water, and which thus controls the copper leaching rate of the paint (equation No. 4, Chapter 16). The greater the rate of solution of the matrix, the lower the toxic loading required to give an adequate leaching rate. Table 14 of Chapter 16 shows the matrix solution rates which are required to give a copper leaching rate of 10 μg./cm.^{2}/day at various loadings of cuprous oxide, and also the weight and thickness of paint required for a life of one year.

Since it is difficult to measure matrix solution rates, and comparatively simple to measure copper leaching rates, the latter are used in evaluating the effect of changes in the formulation. Frequently the ingredients used in the matrix are selected by necessity, depending upon their availability and cheapness, and the problem is one of combining them in the proper proportions and determining the appropriate loading of toxic to give adequate antifouling performance.

The Vehicle

The rate of solution of the matrix and the physical properties of the paint film depend largely upon the choice of the resinous ingredients of the vehicle. Rosin, or some similar soluble resin, must be present in appreciable quantities to insure an adequate solution rate. Neutral resins are added, both to reduce the rate of solution of the rosin and to improve the physical properties of the paint film, which would otherwise be too brittle. Information on the effects of adding various neutral resins to rosin on the solution rate of the mixture has been given in Chapter 17. The amount of neutral resin required to depress the solution rate by a given amount differs with each neutral material. The hard neutral materials cause a greater depression of the solution rate of rosin than do the softer ones. A limiting concentration in rosin, beyond which little or no solution from the mixture can be observed, may be determined for each neutral resin. It follows from these generalizations that plasticizers, which are soft, may be added in considerable amounts without excessive depression of the leaching rate of the paint. The solid resins or synthetic plastics, which may be added to toughen the film, must be used more sparingly to avoid reducing the solution rate of the matrix excessively.

The development of the best combination of ingredients to give optimum performance becomes more complicated as the number of ingredients is increased. Examples for the purpose of this section have been drawn from experiments with the Navy wood-bottom formulation 16X, Navy Department Specification 52-P-61, (*6*). This paint is a simple example since it contains few matrix ingredients and only two pigments. The basic formula of this paint is as follows:

Ingredients	*lb./100 gal.*	*% Dry Paint*
Rosin WW	311	26
Hydrogenated methyl abietate	156	13
Cuprous Oxide	622	52
Diatomaceous silica	104	9
Solvent, Coal Tar Naphtha	92	
Mineral spirits	104	
Total Pigment Volume=26%		
Toxic Volume=17%		

In many experiments, the matrix has been modified by substituting other plasticizers for hydrogenated methyl abietate, by varying the plasticizer-rosin ratio, and by adding various solid resins as tougheners. The pigmentation has been varied by substituting other nontoxic pigments for diatomaceous silica, and by varying both the total pigment volume and the proportion of cuprous oxide to total pigment. These experiments demonstrate that the original formulation, which has excellent fouling resistance but poor physical properties, can be greatly improved.

Selection of type and amount of plasticizer: The following materials have been substituted for the abietate in the same proportion as in the original formulation: chlorinated diphenyl, tricresyl phosphate, dehydrated castor oil, coumarone-indene resin, tall oil and various of its derivatives, bodied fish oil, and linseed oil. Though many of these paints gave perfect fouling resistance for six or eight months, most of them had failed before a year of exposure.

Table 7 presents a summary of the results observed with these paints after eight months of exposure at Miami, when the paints were rated for fouling resistance and for the condition of the paint film.[1] The paint condition ratings varied from 77 to 98 per cent, and the fouling resistance from 52 to 100 per cent, at this time. Only three

TABLE 7. Summary of Fouling Resistance and Physical Condition after 8 Months' Immersion at Miami of Paints in Which Various Plasticizers Have Been Substituted for Hercolyn

Plasticizer	*No. of Exposures*	*Fouling Resistance* %	*Paint Condition* %	*Reasons for Physical Failure*
Tricresyl Phosphate	1	100	90	Al, Ch
Tall Oil	1	100	89	Al
H.M. Abietate	4	95	92	Cr, Ch, W
Bodied fish oil #1	1	90	98	Cr, Ch
Chlorinated diphenyl	2	87	95	Al, Ch
M. Abietate	1	88	95	Ch
Bodied Fish Oil #2	1	83	95	Ch
P.E. Tall Oil Est.	1	75	80	Ch
Coumarone-indene resin	1	76	77	Cr
Dehydrated castor oil	1	75	75	Cr, Ch
Bodied Linseed Oil	1	53	95	Ch
Glycerine Tall Oil	1	52	83	Al, Cr

Al=alligatoring Ch=chipping Cr=cracking W=wearing

of the plasticizers gave paints which were rated above 90 per cent in both fouling resistance and physical performance; namely, tricresyl phosphate, hydrogenated methyl abietate and bodied fish oil. It is apparent that some of the materials tested are unsatisfactory as plasticizers of this composition in the proportion tested. Our experience has further indicated that similar tests must be made to determine the best plasticizer for each different vehicle contemplated in any developmental or improvement program.

[1] The rating system used at Miami is described in the Appendix of Chapter 20.

TABLE 8. Fouling Resistance Ratings of Paints Containing Difference Proportions of Various Plasticizers

Ratio Rosin:Plast.	*Fouling Resistance after 8 Months at Miami, %*			
	A	*B*	*C*	*D*
5:1	100	100	100	81
3:1	100	100	91	69
2:1	100	100	52	75
1:1	100	100	0	0
0.5:1	100	100	0	0

A—H.M. Abietate
B—Tall Oil, Purified
C—Glycerine Tall Oil Ester
D—P.E. Tall Oil Ester

The amount of plasticizer required to give the best fouling and physical performance of 16X was tested by varying the ratio of rosin to plasticizer in the paint film. The plasticizers used were the specified abietate, tall oil, and two tall oil derivatives. The tall oil derivatives gave unsatisfactory fouling resistance in the previous experiment when substituted for the abietate in the original formula. The proportion of the abietate or of purified tall oil had little effect, since all paints made with these plasticizers gave perfect fouling resistance for a period of 8 months (Table 8). The glycerine tall oil, which gave the poorest performance in the experiment of Table 7 at the normal rosin: plasticizer ratio of 2:1, gave perfect fouling resistance for 8 months if the rosin was increased to give a ratio of 5:1. Increasing the rosin mixed with the pentaerithrytal tall oil ester also improved the fouling resistance of the paint, though even the one containing five parts of rosin to one of this plasticizer did not give perfect results. It is clear that both of these esters destroy the fouling resistance of the paint when used in excessive amounts, presumably because of the resultant depression of the solution rate of the matrix.

These experiments show that the proportion of abietate is not critical in the formulation, and that the appropriate proportion of other plasticizers should be determined before comparing the results with those of abietate-containing paints.

Selection of type and amount of toughener: The continued use and testing of 16X showed that the paint film was too soft to give the best performance. The film has therefore been strengthened by the addition of resins of high molecular weight as tougheners. Several experiments showed that the addition of such tougheners had little or no effect on the fouling resistance or physical performance of the paint on static panel tests. An example of these data is given in Table 9, in which the fouling resistance and paint condition of the untoughened formulations are compared with the averages of the results of all of the toughened formulations

TABLE 9. Performance of Toughened and Untoughened Paints Exposed on Steel Panels for 8 Months at Miami, Florida

Plasticizer Used	*Fouling Resistance* %	*Paint Condition* %
H.M. Abietate—untoughened	97 (93–100)	93
H.M. Abietate—toughened, average	93 (80–100)	92
Tricresyl Phosphate—untoughened	100	90
Tricresyl Phosphate—toughened average	89 (73–100)	91
Chlorinated diphenyl—untoughened	89	95
Chlorinated diphenyl—toughened, average	88 (66–100)	95
Bodied fish oil—untoughened	90	98
Bodied fish oil—toughened, average	84 (79–92)	98
Coumarone-indene resin—untoughened	77	100
toughened, average	70 (34–88)	94

studied. In most cases the use of a toughener has had negligible results on these properties of a paint. On high-speed boats, or on the rotating discs used to simulate conditions on such boats (7, 8), however, the toughened paints give much more satisfactory service than the untoughened paints. The results of one such test, studying three tougheners in combination with four plasticizers, are given in Table 10. The use of a toughener in these paints may double or triple their resistance to rapid motion through the water.

TABLE 10. Resistance to Cold Flow of Various Modifications of 16X After Drying 24 Hours and Stationary Immersion in the Sea of 55 Hours. Tested on Primed Steel Discs, 14″ in Diameter Rotated at 500 R.P.M. for 96 Hours

	*Resistance to Flow**			
Plasticizer	*A*	*B*	*C*	*D*
H.M. Abietate	36	87	97	87
Chlorinated diphenyl	48	97	96	97
Coumarone-indene resin	36	96	94	83
Bodied fish oil	31	94	96	91

Tougheners used A—none
B—Chlorinated rubber
C—Cyclicized synthetic rubber
D—Benzyl cellulose.

* Arbitrary scale, 100=perfect performance with no flow. The drying treatment was selected as being a combination of times which would be commonly encountered in service. The effects of drying and stationary immersion on the performance of the paints has been described elsewhere (7, 8).

The effect of varying the proportion of the toughener on both the fouling resistance on static test panels and on the resistance to flow on rotating discs is shown for two tougheners in Table 11. Increasing the amount of benzyl cellulose decreased the fouling resistance of the paint progressively, whereas the paints containing the three highest amounts of chlorinated rubber gave the best fouling resistance of the series. Both of the tougheners improved the resistance to flow, most of the improvement being observed with the addition of a small amount of toughener. For any given formula, determination of the best substance to use as a toughener must be made, since the toughener may not give equivalent results in different vehicles.

TABLE 11. Effect of Varying the Amount of Toughener in the Paint on the Fouling Resistance at Miami, and on the Resistance to Flow when Rotated on Primed 14″ Steel Discs Rotated at 800 R.P.M. in Sea Water

Toughener % by Wt. of Dry Paint	*Fouling Resistance 8 Months* %	*Resistance to Flow* %
0*	92	15
1.7*	91	60
3.4*	84	90
4.9*	82	90
6.1*	73	100
0#	76	23
1.7#	87	71
3.4#	93	96
4.9#	92	96
6.1#	92	99

* Benzyl Cellulose in paint plasticized with H.M. abietate.
# Chlorinated rubber in paint plasticized with coumarone-indene resin.

These examples of studies designed to select the best combination of ingredients in a simple formula are merely illustrative of the approach which may be followed. With the vast number of potential ingredients available, it is clear that these experiments could be greatly extended. Familiarity with the properties of the materials used, and their possible action in the paint, is acquired only by long experience.

Pigmentation

The original pigmentation of 16X was selected arbitrarily. The amount of cuprous oxide used was similar to that in other formulations which had been found to give adequate fouling resistance; the diatomaceous silica was added to minimize the settling and caking of the pigment on the storage of the paint. Investigations of the pigmentation of this formulation have included variations of the total pigment volume obtained both by varying the amount of cuprous oxide and the proportion of cuprous oxide and diatomaceous silica. Substitutions of various other nontoxic pigments for the silica have also been made.

Selection of total pigment volume and amount of toxic pigment: To determine the optimum total pigment volume for this formulation, paints were made containing 12, 18 and 24 per cent pigment volume. Each of these pigment volumes was obtained with various combinations of cuprous oxide and diatomaceous silica as the cuprous oxide ranging from 2.4 to 24 per cent by volume in the various paints.

The paints containing the higher volumes of cuprous oxide were the most effective in preventing the attachment of fouling. None of the paints which contained less than 8 per cent cuprous oxide by volume gave satisfactory fouling resistance after 10 months' immersion at Miami Beach, Florida. Only three of the paints gave 100 per cent

fouling resistance at this time, and these contained 18, 19.2, and 24 per cent cuprous oxide by volume. Lower toxic pigment volumes gave progressively poorer results, as shown in Table 12. The presence or absence of diatomaceous silica appears to have a negligible influence on the fouling resistance of the formulation.

As the total pigment volume of this formulation is increased, the physical condition of the paint appears to improve slightly. Thus, the average condition of the paint film, after 10 months' immersion, for pigment volumes of 12, 18, and 24 per cent, are 80, 86, and 88 per cent, respectively. There is no evidence that the proportion of silica to cuprous oxide has any influence on the physical performance of the paint in any of the groups containing the same pigment volume.

Type of nontoxic pigment: Babel (*1*) has shown that a wide variety of nontoxic pigments give satisfactory results in a copper antifouling paint. Others, however, which included talc, clay, mica, and surface-treated precipitated calcium carbonate, showed less promise. Similar results have been found in our experiments with 16X.

The effect of substituting various nontoxic pigments for diatomaceous silica in the 16X formulation was investigated in another experiment. Several extender pigments were found to give better physical performance and better fouling resistance than the silica after six months of immersion. Zinc oxide, Venetian red, and Indian red all gave 100 per cent fouling resistance during the first 6 months of exposure, compared to a fouling resistance of 90 per cent for the paint containing the silica. Only one of the extenders was appreciably poorer than the silica, namely, precipitated chalk. With the exception of precipitated chalk all of the extenders tested gave somewhat better physical performance than the silica during the 6 months' exposure. The results of this experiment are summarized in Table 13.

To investigate whether a combination of two extender pigments would have more virtue than one alone, zinc oxide was substituted for various amounts of the extender pigments used in the previous experiment. Its presence appeared to have beneficial effects only when combined with precipitated chalk which, as shown above, gave poor results when used alone. In the other paints there was no consistent indication that the presence of zinc oxide was beneficial.

With regard to the appropriate pigmentation of 16XM, these experiments show that a pigment volume of 24 per cent and a toxic volume of 16 per cent or more give the best results. A paint containing 24 per cent cuprous oxide by volume is satisfactory but probably wasteful. The silica may be increased to as much as one-third of the total pigment without detriment to the performance of this paint. Though diatomaceous silica is satisfactory it does not appear to be as good as magnesium silicate, Venetian red, Indian red, zinc oxide, or barytes. It is appreciably better than precipitated chalk.

TABLE 12. Fouling Resistance and Condition of the Antifouling Paint Film of Paints Containing Various Amounts of Silica and Cuprous Oxide after 10 Months' Immersion at Miami Beach, Florida

Total Pigment Volume, %	*Cu_2O Volume, %**	*Fouling Resistance %*	*Paint Condition %*
12	12	80	75
	9.6	75	82
	8	75	80
	6	84	85
	4	**	**
	2.4	**	**
18	18	100	90
	14.4	91	82
	12	83	82
	9	35	90
	6	**	**
	3.6	**	**
24	24	100	88
	19.2	100	91
	16 (16XM)	93	85
	12	94	90
	8	85	88
	4.8	0	88

* Remainder of pigment is diatomaceous silica.
** Test terminated after 7 months because of severe fouling on the panel.

The various experiments described show that the original formula 16X can be greatly improved. Although its resistance to fouling is excellent, its physical properties are too poor for prolonged service on fast boats. The resistance to water erosion can be improved greatly by adding a toughening agent to the film. Changes in the composition of the pigment may also improve both the physical and antifouling properties of the paint.

The experiments presented in this chapter are merely illustrative of the types of investigation necessary to study a formulation. A brief review of the principal questions which require investigation may be useful.

TABLE 13. Effect of Substituting Various Pigments for Diatomaceous Silica on the Fouling Resistance and Condition of the Antifouling Paint Film After Exposure for Six Months at Miami Beach, Florida

Pigment Used	*Fouling Resistance* %	*Paint Condition* %
Diatomaceous silica	90	85
Magnesium silicate	93	100
Venetian red	100	90
Indian red	100	89
Zinc Oxide	100	88
Barytes	95	90
Precipitated Chalk	50	84

In the design of a paint with an insoluble matrix it is necessary to determine: 1.) the volume loading of toxic required to insure adequate leaching rates, and 2.) the optimum pigment volume for adequate physical performance. The vehicle used must be tough enough to form an adequate binder for the volume of pigment required.

In the design of a paint with a soluble matrix, the volume of toxic required to insure adequate leaching rates will vary inversely with the rate of solution of the matrix. For any given paint the volume of toxic and the total pigment volume to give optimum results must be determined. To select the matrix composition, variations in the proportion of soluble resin to insoluble resins should be studied. An increase of plasticizers will cause less decrease in the rate of solution of the matrix than will an equal increase of harder materials used to toughen the film. Appropriate juggling of these three constituents will give a matrix of any desired solution rate, within limits, and the pigment content of each matrix will vary accordingly.

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