

Mechanism of Release of Toxics from Paints

There is considerable evidence that the anti-fouling action of paints is determined by the rate at which copper or other toxics are liberated from their surface into sea water. This evidence has been reviewed in Chapter 14. The rate of release, or leaching rate, depends not only upon the solubility and rate of dissolution of the toxic, discussed in the preceding chapter, but also upon how it is compounded in the paint.

The purpose of this chapter is to review the leaching behavior of antifouling paints, and to discuss the mechanism which may permit a paint to maintain the leaching rate at an effective level without exhausting too rapidly the store of toxic.

The leaching rates of paints change with the time of immersion in the sea. As long as the copper is released at a rate greater than $10 \mu\text{g./cm.}^2/\text{day}$, fouling is prevented. Some paints maintain an adequate leaching rate for a considerable period of time, whereas the leaching rates of others fall to inadequate values in a relatively short period.

The leaching rates of certain successful paints decrease steadily from an initial high value. Such a paint may have an adequate leaching rate for many months, and is conveniently characterized

by the time at which the leaching rate falls below the critical value. Certain other effective paints have leaching rates which, after the first few weeks' immersion, remain nearly constant for many months, and then finally drop to inadequate values. Such a paint can be characterized not only by the time at which the leaching rate falls below the critical value, but also by the leaching rate level which is maintained for the greater part of its

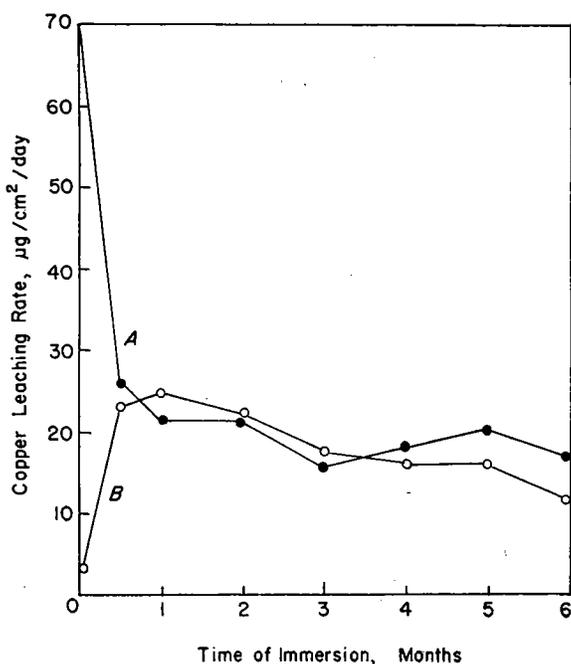


FIGURE 1. Change of leaching rate with time of immersion in the sea, for two paints whose leaching rates are initially widely divergent but nearly the same after a short period of soaking.

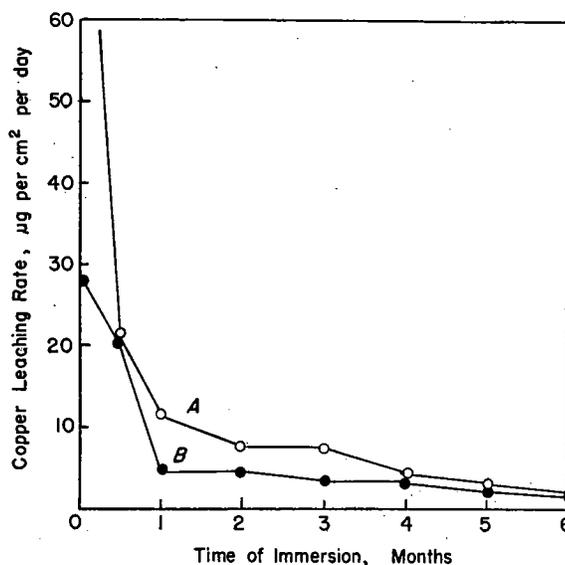


FIGURE 2. Leaching rates of paints which show rapid exhaustion of toxic in sea water, plotted against the time of immersion in the sea. The initial leaching rate for the paint represented by Curve A is $143 \mu\text{g./cm.}^2/\text{day}$.

life. This level is called the "steady-state leaching rate."

The various types of behavior of antifouling paints can be illustrated by curves showing changes in leaching rate after immersion in the sea.

Figure 1 shows that two paints which have very different initial leaching rates may leach at nearly identical rates after a short period of soaking in the sea. One of the paints (Curve A) has a high initial rate, which decreases during the first month of soaking to a value of about $20 \mu\text{g./cm.}^2/\text{day}$ and then fluctuates about this value for the remaining five months of exposure. The other (Curve B) has a low initial rate, which increases during the first two weeks of exposure to a value of about $25 \mu\text{g./cm.}^2/\text{day}$ and then falls gradually during the remaining exposure period. The *initial* leaching

rates of these paints give no indication of their ability to maintain an adequate leaching rate during a long period of exposure.

Another type of behavior is illustrated in Figure 2. The leaching rates fall sharply soon after immersion and reach inadequate values within two months. Such behavior may result from an inadequate supply of toxic in the paint film, which

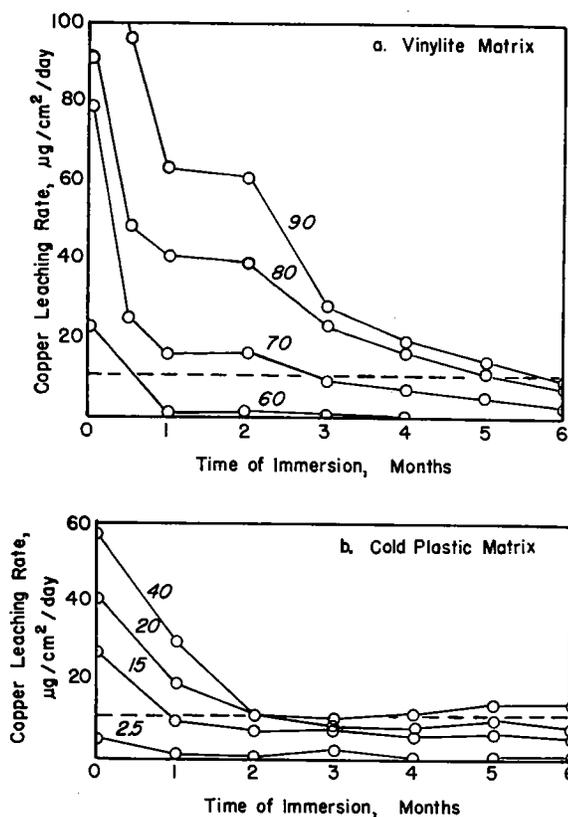


FIGURE 3. Leaching rates of paints containing various amounts of cuprous oxide, in two different matrices, plotted against the time of immersion in the sea. Figures refer to the cuprous oxide content as per cent dry weight of the paint film.

becomes exhausted within a short interval, or to properties of the film which do not permit the continued release of the toxic. Curve A shows the leaching rates of a metallic copper paint which had the high initial leaching rate of $143 \mu\text{g./cm.}^2/\text{day}$. The total amount of copper initially present in the film amounted to only $3,228 \mu\text{g./cm.}^2$. Of this, $1,292 \mu\text{g./cm.}^2$, or 40 per cent, was lost during the first month of immersion in the sea. It is not surprising, therefore, that the leaching rate decreased to an inadequate value by the second month of immersion. Curve B shows the leaching rates of a cuprous oxide paint which became inadequate during the first month of soaking although most of the toxic still remained within the paint film. Some paints never have adequate leaching rates, and foul when first immersed.

The ability of a paint to maintain an adequate uniform leaching rate for a substantial period depends primarily upon the character of the matrix, which determines the mechanism controlling the release of the toxic. This, in turn, defines the general character of the leaching rate curves, particularly the way leaching changes with time. For any given matrix, the amount of toxic incorporated in the film determines the actual rate at which copper will be liberated at any given time. Figure 3 shows the results obtained with two series of paints made with different matrices to which varying amounts of cuprous oxide were added.

In the series of Figure 3a, the matrix was Vinylite. The leaching rates of all the formulations were initially high, but fell steadily during prolonged sea exposure. The time elapsing before the leaching rate fell below $10 \mu\text{g./cm.}^2/\text{day}$ decreased regularly as the percentage of copper in the paint became smaller, being six months for the paint containing 90 per cent cuprous oxide, compared to two weeks for the paint containing 60 per cent.

In the series of Figure 3b, the matrix was a cold plastic. The leaching rates of all the paints were initially high, but fell during the first two months of soaking and attained fairly steady values which were maintained for the duration of the experiment. The steady-state values for the paints containing 20 per cent and 40 per cent cuprous oxide were adequate; for those containing 15 per cent and 2.5 per cent cuprous oxide, inadequate.

The leaching behavior of paints is readily divided into initial leaching rates and steady-state leaching rates. The initial leaching rate represents one property of a paint system. The change of leaching rate with time during immersion is another characteristic which bears no obvious relation to the initial value. If the leaching rate falls steadily throughout immersion, the *time* at which it drops below the critical value characterizes the useful life of the paint. Finally, if a steady-state leaching rate is attained after a period of soaking, its value is of primary importance in practical performance.

The initial leaching rate depends solely upon the nature of the *surface* of the fresh paint, which has transitory properties of little value in determining the effectiveness of the paint in preventing fouling. The steady-state leaching rate depends upon the release of toxic from the *interior* of the paint film. The most important aspect of the leaching behavior of paints is the mechanism which makes the deeper stores of toxic in the paint available to the solvent action of sea water.

INITIAL LEACHING RATES

A surface freshly coated with antifouling paint is covered with irregularities where the particles of toxic project from the solidified matrix. Depending upon the degree of dispersion of the pigment, the protruding toxic may be in the form of individual toxic particles, or of aggregates which are considerably larger.

Since paint vehicles wet the pigments suspended in them, it might be expected that each projecting toxic particle would be covered by a very thin layer of matrix. Actually, most antifouling paints begin to leach immediately, or at least within a few minutes, after immersion in sea water, so that any such skin of matrix must ordinarily be too thin to interfere with the dissolution of the toxic, or is rapidly removed after immersion. It is only in the case of certain compositions, particularly those applied as melts rather than with solvents, that a matrix skin delays the dissolution of toxic particles. This behavior will be discussed in more detail below.

In the typical antifouling paint, leaching begins at once when the fresh surface is immersed in sea water, and the protruding toxic particles begin to dissolve. The *initial* leaching rate at this moment depends on two factors: (A) the intrinsic rate of solution of the toxic at the prevailing temperature, salinity, and pH; and (B) the area of toxic exposed. These two factors will be discussed separately. Although the treatment is applicable for any toxic, it is given here specifically for cuprous oxide, and the experimental data refer to cuprous oxide paints.

The Intrinsic Rate of Solution

The dependence of the rate of solution of cuprous oxide upon different physical and chemical variables has already been described in Chapter 15. It is useful to review these data briefly.

1. The rate of solution is proportional to the hydrogen ion concentration.

2. The rate of solution is proportional to the square of the chloride ion concentration (at constant ionic strength).

3. As the ionic strength is increased, at constant chloride concentration, the rate of solution at first decreases, and then changes relatively little.

(These first three variables need not be considered when the solvent is normal sea water, since the pH, chlorinity, and ionic strength are fixed.)

4. The rate of solution increases with temperature, following the Arrhenius equation. In the neighborhood of 20°C. the increase amounts to three per cent per degree.

5. Relative values of the rate of solution can be measured only if the agitation of the solvent past the surface is high enough so that diffusion has a negligible effect in limiting the rate of solution.

The Area of Exposed Toxic

The above discussion of the rate of solution of cuprous oxide concerns relative values only. The absolute value of the intrinsic rate of solution, or rate per unit area of exposed toxic, is practically impossible to measure, because that area cannot be accurately determined, or even estimated. The measured leaching rate is calculated on the basis of the geometrical area of the paint surface considered as a plane. It may be in general either greater or less than the intrinsic rate of solution, depending on whether the actual area of toxic is greater or less than the geometrical surface area. The actual area may be greater because of protruding particles and surface irregularities, or less because part of the surface is covered by matrix.

The rate of dissolution of toxic into a given volume of solvent is proportional to the geometrical area of the paint (Chapter 15, Figure 11). It is natural to assume that, similarly, on a microscopic scale, the measured leaching rate is proportional to the actual area of toxic exposed. If this is true, we should expect the relation

$$L = k \frac{a}{A} \quad (1)$$

where L is the measured leaching rate, k the intrinsic rate of solution (i.e., the leaching rate of a plane surface of pure cuprous oxide), a the actual area of toxic exposed, and A the geometrical area of the surface considered as a plane.

The concept of exposed toxic particles projecting from a matrix surface is illustrated in Figure 4.

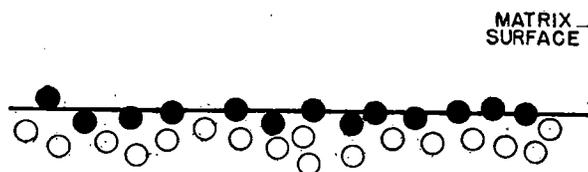


FIGURE 4. Illustration of the concept of surface-exposed toxic. The black circles represent toxic particles exposed on the surface and immediately available for dissolution.

The surface-exposed area, a , is the sum of the individual exposed areas, some large, some small, depending on the extent of protrusion. In practice, of course, the cuprous oxide particles have irregular shapes and vary in size, instead of being uniform spheres as shown.

In soluble matrix paints it has been found that

the smaller the cuprous oxide particles, the greater the initial leaching rate. The steady state leaching rate, however, was independent of particle size within the limits studied (2).

The fundamental assumption expressed by equation (1) is the basis upon which a large body of data on initial and steady-state leaching rates has been interpreted. There is no experimental evidence which conflicts with this assumption.

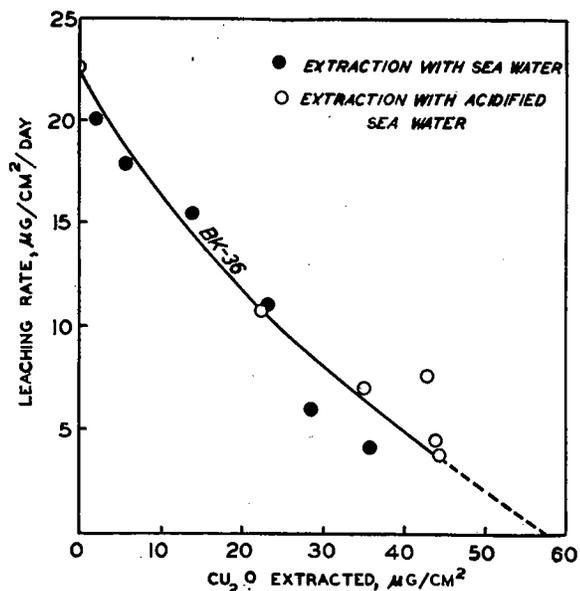


FIGURE 5. Leaching rates in normal sea water of an antifouling paint after extraction of surface exposed toxic in normal and in acidified sea water. The paint contained 40 per cent cuprous oxide in a rosin Vinylite matrix.

The Initial Amount of Exposed Toxic

If the particles were uniform spheres, the maximum amount of toxic which could be exposed on a freshly-painted surface would be represented by hexagonal close packing of a single layer of spheres. The mass per unit area of such a layer is $1.21 r\rho$, where r is the particle radius and ρ the density. For electrolytically prepared cuprous oxide, r is roughly 1 micron,¹ and ρ is about 6 g./cc. The maximum initial amount of surface-exposed toxic might therefore be expected to be of the order of 700 $\mu\text{g./cm.}^2$

The amount of surface-exposed toxic can be determined experimentally by extraction under conditions where the matrix is not attacked,

¹ The particle sizes in commercial cuprous oxide vary widely from one sample to another another, and there is also a distribution of sizes in any one sample. Electrolytically prepared cuprous oxide ordinarily has a smaller average size, and also less size heterogeneity, than does pyrochemical cuprous oxide. The size distributions and specific surface areas of representative samples of electrolytic cuprous oxide have been estimated from photomicrographs by the Mare Island investigators (27). The particle radius which, for a hypothetical homogeneous sample, would give the same specific surface area varied from 1 to 2 microns,

provided there are no contacts between surface particles and those lying beneath them (3, 10, 13). In the case of an insoluble, inerodible matrix, the extraction may be carried out either in ordinary sea water or in acidified sea water, which hastens the process. Measurements of the leaching rate under standard conditions at intervals during the extraction show a gradual decrease, indicating that the total area of exposed toxic diminishes, as would be expected. An example of this procedure is shown in Figure 5 for a paint containing 40 per cent of cuprous oxide, 30 per cent of Vinylite, and 30 per cent of rosin extracted both in normal sea water and in sea water acidified to pH 3.9 with citric acid. The results of the two solvents are in good agreement. The leaching rate approaches zero when 57 $\mu\text{g./cm.}^2$ of cuprous oxide have been extracted; this represents the amount initially exposed on the surface. In the case of a matrix which is soluble in normal sea water, it is necessary to extract the toxic with another solvent; acidified sea water is often satisfactory. As described in a subsequent section, the amount of surface-exposed cuprous oxide on a cold plastic paint containing 40 per cent of toxic by weight has been determined in this way to be 240 $\mu\text{g./cm.}^2$ (Figure 13).

It is reasonable that both these experimental values should be considerably smaller than the estimated maximum corresponding to a closely-packed surface. The fact that they are not identical, even though the two paints contained the same proportion of cuprous oxide, indicates that the concentration of toxic at the surface of a fresh paint film may be different from its concentration in the film interior—a well-known phenomenon in paint technology. In some cases the pigment may tend to accumulate at the surface, so that the initial amount of exposed toxic approaches that of a closely-packed surface even for a paint in which the toxic loading is not particularly high. In others, the matrix or one of its components may tend to accumulate at the surface. These abnormal surface concentrations would naturally cause the initial leaching rate to be abnormally high or low, respectively.

Depression of the Initial Leaching Rate by a Surface Skin of Matrix

The leaching rates of some paints are initially abnormally low and rise after immersion for a few hours or days in sea water. This phenomenon is ascribed to the accumulation of a thin skin of matrix (or one of its components) over some or all of the toxic particles at the surface.

The likelihood of the presence of a matrix skin on a freshly painted surface was discussed by Ragg (29) in 1925. Unlike many previous authors, he was convinced that the skin was ordinarily removed soon after immersion. He showed that a panel coated with a paint compounded of varnish and cuprous thiocyanate did not release toxic into sea water, but that by exposure to agitated or flowing sea water the surface was unsealed and the toxic was permitted to dissolve.

In recent investigations, the effects of a surface skin, or a low surface concentration of toxic, have been noted particularly in the case of hot plastic paints. Here the skin is believed to be formed dur-

TABLE 1. Leaching Rates* of Hot Plastic Paints

Treatment of Surface	Leaching Rate after Immersion in the Sea				
	0 wk.	1 wk.	2 wks.	1 mo.	2 mos.
None	1.7		9.2	13.4	17.5
Buffed	33.9		14.3		10.3
None	2.8	20.9		16.1	9.4
Buffed	48.3	19.3		12.9	12.3

* $\mu\text{g./cm.}^2/\text{day}$

ing the solidification of the melt. It can be removed by sandpapering or buffing, with consequent rise in the initial leaching rate. Examples of low initial leaching rates of hot plastic paints and the effect of buffing are given in Table 1, which shows also that the normal leaching rate is regained rather slowly by soaking in sea water. The abnormally low initial leaching rate can be raised if the paint is applied dissolved in a solvent instead of a melt (without otherwise changing its composition).

That the surface skin on fresh coatings of hot plastic paints is composed largely of the paraffin which such paints contain is indicated by visual examination and also by the wetting behavior of the surface. The contact angle between water and air at the paint surface (15) is about 101° , close to that of paraffin (1), 105° . As a hot plastic paint is soaked for several days in sea water, the contact angle falls to about 15° , representing a marked improvement in the degree of wetting of the surface (15).

In other cases, the surface skin of matrix seems to be removed much more rapidly by sea water, so that its presence is inferred only from an abnormally low leaching rate for the first hour or so after immersion. For example, Table 2 gives leaching rates for paint 16X (containing cuprous oxide, Celite, rosin, and Herculyn) calculated for the first and second hours of immersion. The leaching rate is low at first, and almost doubles after one hour's immersion. This behavior is characteristic of paint 16X (as well as some cold plastics), sug-

TABLE 2. Leaching Rates* of Paint 16X

Cuprous Oxide Sample	Panel No.	Period	Period
		0-1 hr.	1-2 hr.
87	A	32	80
87	B	24	62
88	A	32	46
88	B	30	50

* $\mu\text{g./cm.}^2/\text{day}$

gesting that the Herculyn-rosin mixture forms a thin skin which is removed very soon after immersion in sea water.

Significance of the Initial Leaching Rate

The leaching rate of a freshly exposed cuprous oxide paint can be either abnormally high or abnormally low. If there is accumulation of toxic in the surface, the initial leaching rate will be high and will drop after the surface excess has dissolved. This is the interpretation of Curve A in Figure 1. If there is a surface skin of matrix, or an abnormally low surface concentration of toxic, the initial leaching rate will be low and will rise after the skin has been removed, until a steady-state rate is established. This is the interpretation of Curve B in Figure 1.

When there is no toxic available for dissolution except that originally exposed on the surface, the behavior shown in Figure 2 is found. In general, this may result either from a matrix which is insoluble, impermeable, and ineredible, or from an extremely thin paint film in which there is only one layer of toxic particles so that all of the toxic present is exposed at the surface.

The transitory nature of the initial leaching rate may be emphasized by noting the ratio of the mass of surface-exposed toxic to the initial leaching rate. This ratio gives the time the toxic would last if the initial rate persisted. In the Vinylite paint described in Figure 5, it is $(57 \mu\text{g./cm.}^2)/(22 \mu\text{g./cm.}^2/\text{day})$, or about $2 \frac{1}{2}$ days. Clearly, the original surface-exposed toxic is exhausted rapidly. If, therefore, a paint is to continue to leach over a period of months, it must do so through dissolution of toxic particles deep in the interior of the paint.

The initial leaching rate is thus never a criterion of the performance of a paint in service. However, measurements of initial leaching rates are useful for studying the phenomena of surface accumulation and of matrix skin formation. Another possible application of initial leaching rate measurements is in the testing of toxic samples; comparative measurements of the rates of solution of different lots of cuprous oxide may be made by compounding them under carefully controlled conditions in the same matrix.

STEADY-STATE LEACHING RATES

After the first few weeks, in which rapid changes in the leaching rate occur, the rate may either decrease gradually throughout a prolonged period of immersion or may remain nearly constant. (See Figure 3.) The term "Steady-state leaching rate" may be applied to the condition which prevails after the first few weeks of soaking in sea water, although it is not always strictly true that no change in rate is taking place.

The toxic originally exposed at the surface is exhausted within a few days after immersion. If the toxic in the interior is permanently locked up in the matrix, there is no further leaching; the steady-state leaching rate is zero. If, on the other

Class Two: Removal of toxic and matrix
 By dissolution of the matrix
 By bacterial action on the matrix
 By mechanical erosion of the matrix

Before discussing the mechanisms in detail, it is of interest to contrast the two general classes of steady-state leaching by presenting data on the changes in composition of paints over long periods of soaking.

Changes in composition during soaking: If toxic alone is removed, the toxic content of the paint film will steadily decrease. Ideally, the loss of weight of a unit area of paint film should be equal to the loss of toxic, and the latter should be given by the integral of the leaching rate over the soaking

TABLE 3. Changes in Composition of Vinylite Paints During 3 Months' Soaking in the Sea (15)

Paint No.	Original Composition, %				Cu ₂ O, %		Weight of Cu ₂ O lost, μg./cm. ²
	Vinylite	Rosin	Celite	Cu ₂ O	In Residual Paint	In Material Lost*	
1	10	0	0	90	76	130	3,900
3	20	0	0	80	71	109	1,600
4	15	5	0	80	57	106	3,200
7	30	0	0	70	53	187	1,200
8	22.5	7.5	0	70	47	125	1,700
13	12.9	4.3	12.8	70	54	106	3,500
14	15	0	15	70	60	132	2,000
17	17.3	5.7	17	60	37	123	2,500
21	21.6	7.2	21.2	50	34	101	1,600

* Calculated by difference.

hand, the toxic is made available for dissolution from the interior of the paint, there is a finite steady-state leaching rate, and its value at any given time is proportional to the area of toxic exposed at that moment.

The interpretation of steady-state leaching rates, and their practical control in formulating paints, depend upon an understanding of the mechanism for release of toxic from the paint interior. This is, in fact, the basic problem of anti-fouling paint technology. There are five different possible mechanisms of release which have been discussed in the literature and studied in recent investigations. There is evidence that different mechanisms operate in different formulations.

The five mechanisms fall naturally into two classes, depending on whether *toxic alone* is removed from the paint in steady-state leaching, leaving a residual skeleton of matrix, or whether *both toxic and matrix* are removed, so that the thickness of the paint film gradually diminishes. The classification is as follows:

- Class One: Removal of toxic alone
 By diffusion through a permeable paint
 By continuous contact of toxic particles

period. This relationship has been quantitatively confirmed for accelerated extraction in the laboratory, but only qualitative confirmation can be expected for sea soaking, because of the formation of surface deposits to be discussed below. If, on the other hand, both toxic and matrix are removed in the same proportions as they are compounded in the original paint, the toxic content of the residual paint film will remain constant. It may decrease slightly if a part of the matrix remains on the surface or if the weight of the paint is increased by deposit formation.

The data which follow are based on the change of weight and copper content of paint films during a period of soaking in the sea. The copper was calculated as cuprous oxide, and the loss of matrix was calculated as the difference between loss of weight and loss of cuprous oxide.

The data recorded in Table 3 are from examples of Class One paints, in which only toxic is removed. Panels painted with formulations containing various amounts of cuprous oxide, Vinylite, rosin, and Celite were immersed in the sea for three months. The paints whose leaching rates are shown in Figure 3a are selected from this group.

Table 3 gives the original composition of each paint, and also the cuprous oxide contents of the residual paint after soaking and of the portion of the paint which was lost in the sea.

The values for weight of cuprous oxide lost show that extraction of toxic has extended past the surface layer (which amounts to not more than about 700 μg . per cm^2 for particles 1 micron in radius), and therefore that dissolution is taking place from the paint interior. The losses amount to from one-third to one-half of the original paint weights. The cuprous oxide content of the residual paint is in every case much lower than that of the original, showing preferential extraction of toxic. The cuprous oxide content calculated for the material lost is in every case at least 100 per cent, indicating that cuprous oxide alone has been removed. The values greater than 100 per cent are probably occasioned by deposit formation, which makes the weight loss appear to be less than the loss of cuprous oxide. This is an example of Class One steady-state leaching which involves the removal of toxic alone.

The data presented in Table 4 are from examples

TABLE 4. Changes in Composition of Cold Plastic Paints During 2 Months' Soaking in the Sea

Paint No.	Content of Cu_2O , %			Total Weight Lost $\mu\text{g. per cm}^2$
	In Original Paint	In Residual Paint	In Material Lost*	
C2	1.4	1.4	1.2	1,300
C3	2.5	2.4	3.9	2,800
C6	15.6	13.6	30.7	2,300
C7	21.8	21.2	25.6	2,300
C10	40.5	39.9	45.6	2,000

* Calculated by difference.

of Class Two paints, in which both toxic and matrix are removed simultaneously (22). It represents a group of cold plastic paints containing various amounts of cuprous oxide in which the pigment volume was kept constant by substituting magnesium silicate for the omitted toxic. The paints whose leaching rates are shown in Figure 3b are selected from this group. Painted panels were immersed in the sea for two months. Table 4 gives the cuprous oxide contents of the original paint, the residual paint, and the material lost. The total weight losses show that the dissolution has penetrated beyond the surface layer of toxic. The toxic content of the residual paint and that of the material lost (except for No. C6) are fairly close to the original toxic content in each case. This is an example of Class Two steady-state leaching which involves the removal of both toxic and matrix in

approximately the same proportions as in the original paint composition.

A schematic diagram of the two classes of steady-state leaching is shown in Figure 6. The removal of toxic alone leaves a matrix skeleton intact (B), whereas the removal of toxic and matrix reduces the thickness of the paint layer (D).

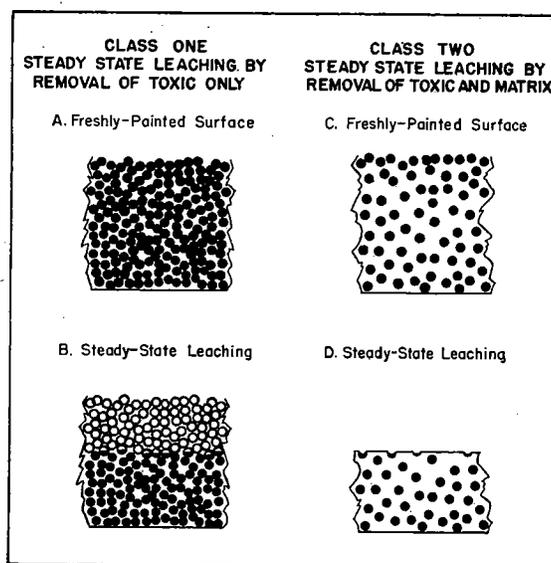


FIGURE 6. Schematic diagram of the two classes of mechanisms for maintenance of steady-state leaching.

MECHANISMS OF CLASS ONE LEACHING

Two possible mechanisms for removal of toxic from the interior of the paint without loss of matrix are: 1) the diffusion of dissolved toxic through a permeable matrix, and 2) the dissolution of toxic particles which are in continuous contact throughout a paint film.

Diffusion Through Permeable Matrices

Several writers (17, 28, 41) have assumed that the mechanism of diffusion operates generally in antifouling paints, and they have discussed its theory. The hypothetical process involves the permeation of water through the matrix into the paint interior, the dissolution of toxic there, the outward diffusion of dissolved toxic, and its release at the paint surface.

There is no doubt that films prepared from the resins of which antifouling paint matrices are composed are all permeable to water to some extent. The rates of diffusion of water vapor through films of various resins have been measured under condi-

tions where a gradient of vapor pressure through the film exists (4). For example, Young, Gerhardt, and Schneider (40) measured the rates of water permeability of several different resins commonly used in paint matrices, and found values ranging from 4 to 300 mg. per sq. in. per day on the basis of a film one mil thick. Similar measurements by Elm (9) gave values (on the basis of one mil thickness) of 70 mg. per sq. in. per day for a film prepared from a phenolic resin vehicle, and 210 for one from an alkyd resin vehicle. These values were diminished somewhat (of the order of a factor of one-half) by incorporation of various pigments.

The operation of steady-state leaching through permeation would presumably involve a quite different sort of process from that studied in the above experiments, however. Instead of diffusion of water vapor along a concentration gradient, we are concerned here with diffusion of salt ions. The transfer of either water molecules or ions through resinous films is probably an activated process (4, 8). It is interpreted as a successive migration on a molecular scale through temporary local voids in the resinous structure which open up from time to time in the course of restricted thermal motions of the resin macro-molecules. The larger the migrating molecule, the greater the energy required to open a passage for it, and the frequency of openings diminishes exponentially with the energy. Since a hydrated salt ion such as the cuprous chloride complex is considerably larger than a water molecule, it might be expected to diffuse more slowly than the latter. At any rate, permeability to water vapor and permeability to ions may be two very different considerations.

There are several sources of experimental evidence that the permeability of some paint matrix films to ions is very small.

Experiments at Woods Hole (5) showed that films of 143E matrix, and of a similar cold plastic matrix termed "rosin vehicle" by the Mare Island Paint Laboratory, with a thickness of about 0.1 mm., were virtually impermeable to cupric chloride and to cupric citrate. Solutions of these salts at concentrations ranging from 10^{-3} M to 0.5 M were employed, the solution being placed on one side of the film in each case, with sea water on the other side. Tests conducted over a period of a hundred days indicated that the rate of permeation, calculated in leaching rate units, was less than $0.01 \mu\text{g. per cm.}^2$ per day. In other experiments, surfaces painted with a cupric citrate paint (which had the enormous leaching rate of $1,300 \mu\text{g. per cm.}^2$ per day) were covered with layers of

different types of matrix (143E, rosin vehicle, Vinylite, and Vinylite-phenolic resin) and then leached in sea water. The amounts of copper liberated in 280 hours corresponded to leaching rates of $0.1 \mu\text{g. per cm.}^2$ per day or less. It was concluded that the permeabilities of these matrices to cupric citrate and cupric chloride were quite negligible.

Experiments reported by Elm (9) showed that a film of a gray alkyd finishing paint can function as a semipermeable membrane which is permeable to water but impermeable to salt ions. In these studies, glass panels were painted with a zinc chromate primer (which contains water-soluble electrolytes) and then covered with the finishing paint. They were immersed for periods up to 35 days in water and in sodium chloride solutions. In water, the paint imbibed considerable amounts of fluid and blistered. In sodium chloride solutions, the amount of fluid imbibed decreased progressively with increasing concentration of salt. Thus the paint system apparently acts as an osmotic cell, in which the under side of the paint represents a solution with high osmotic pressure, and the outer film of alkyd finishing paint represents a semipermeable membrane. When the outside of the membrane is in contact with a solution of lower osmotic pressure than that of the interior, water is forced in. But if the osmotic pressure of the outer solution is increased, the osmotic imbalance is less and there is less imbibition. Elm concluded that no sodium chloride penetrated to the interior of the paint, and that no soluble electrolytes from the primer escaped to the outer solution; thus the outer film was apparently impermeable to salt ions.

On the other hand, Young, Gerhardt, and Schneider (40) have reported that certain other types of matrix, when employed in antifouling paints, permit the leaching of toxic by diffusion from the interior. Such matrices demonstrated quite high permeabilities to water vapor; a correlation between water vapor permeability and salt ion permeability was inferred, although no direct measurements are yet available to test this suggestion.

It may be concluded that a paint matrix must possess rather specialized properties in order to permit steady-state leaching by diffusion of dissolved toxic through the paint film. Since some matrices which are impermeable to ions can nevertheless be used successfully in antifouling paints, it is clear that other mechanisms can operate to maintain steady-state leaching.

Continuous Contact of Toxic Particles

The second possible mechanism for removal of toxic from the interior of the paint without loss of matrix is the consecutive dissolution of toxic particles which are crowded together in continuous contact throughout the paint film. In this process, whenever a particle is dissolved, another is simultaneously uncovered beneath it. Even though the substance of the matrix is quite impermeable, the leaching can proceed and toxic can eventually be removed from deep in the interior of the paint. As the toxic is dissolved, a tenuous skeleton of the matrix substance remains on the surface, with voids where the toxic particles were previously located.

It is obvious that continuous contact of toxic particles cannot be achieved by crowding them together unless the proportion of toxic is very high. Under these conditions, the paint may be expected to be crumbly and noncoherent unless an extremely strong, tough binder is used. In practice, the only matrices which have been used for successful continuous contact paints have been composed largely of synthetic high polymers, such as Vinylite (polyvinyl chloride-polyvinyl acetate

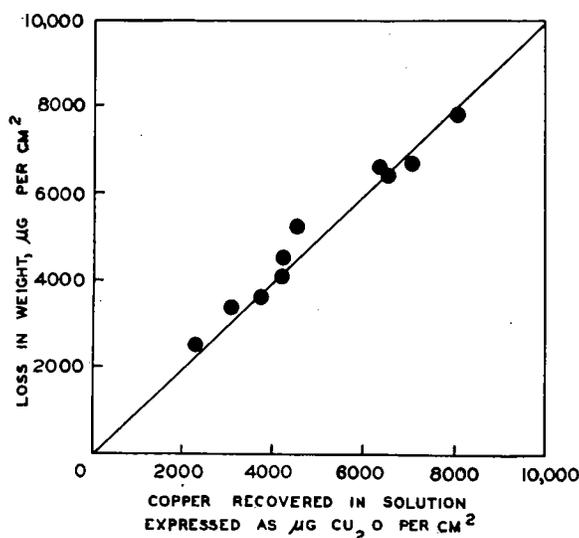


FIGURE 7. Loss in weight of Vinylite paints with cuprous oxide contents of 70 per cent and greater, after extraction in citrated sea water, plotted against copper recovered in solution, expressed as weight of cuprous oxide per unit area.

lated on the basis of cuprous oxide, is compared with the gross loss in weight of the paint (16). The two values are practically identical in each case. The data are also plotted in Figure 7.

Recalling that the maximum amount of cuprous

TABLE 5. Leaching Rates* of Vinylite-Cuprous Oxide Paints after Immersion in Sea Water for Various Periods

BK No.	Composition by Weight		Volume Fraction Cu_2O	Leaching Rate after Soaking in the Sea			
	Cu_2O %	Vinylite %		Initial	1 mo.	2 mos.	3 mos.
1	90	10	0.65	146	64	61	29
3	80	20	0.45	92	41	38	23
7	70	30	0.33	79	16	16	9
30	60	40	0.24	23	0	2	1
31	40	60	0.12	12	1	2	1

* $\mu\text{g./cm.}^2/\text{day}$

copolymer) and polyvinyl butyral. With these binding agents, strong and durable coatings containing as much as 90 per cent cuprous oxide by weight have been prepared (38). The leaching behavior of such systems has several characteristic aspects.

(1) Prolonged steady-state leaching in sea water occurs only if the volume fraction of cuprous oxide exceeds 0.3. This is shown in Table 5, which presents data for the leaching rates of five such paints after immersion in the sea for various periods. A graphical representation of these data has already been given in Figure 3a.

(2) When such a paint is extracted in citrated sea water (to prevent basic cupric carbonate formation), only the toxic dissolves, and the matrix is left behind as an intact skeleton. This is demonstrated in Table 6, where the copper recovered in solution after such extraction, calcu-

oxide in a single surface layer of toxic particles is of the order of $1,000 \mu\text{g. per cm.}^2$, we can conclude that the extraction has extended deep into the interior of the paint. In fact, the paints after ex-

TABLE 6. Extraction of Continuous Contact Paints in Citrated Sea Water. Toxic: Cuprous Oxide; Matrix: Vinylite-Rosin Mixtures Extracted for 34 Days in Sea Water Containing 1 g. Sodium Citrate per Liter

% Vinylite in Matrix	Cuprous Oxide		Recovered in Solution $\mu\text{g./cm.}^2$	Total Weight Loss $\mu\text{g./cm.}^2$
	% in Paint before Extraction	Volume Fraction		
50	90	0.65	8,000	7,900
50	85	0.54	6,400	6,700
50	80	0.45	4,600	5,300
50	75	0.38	4,200	4,600
50	70	0.33	3,100	3,500
75	90	0.65	7,000	6,800
75	85	0.54	6,600	6,600
75	80	0.45	4,100	4,100
75	75	0.38	3,700	3,700
75	70	0.33	2,300	2,500

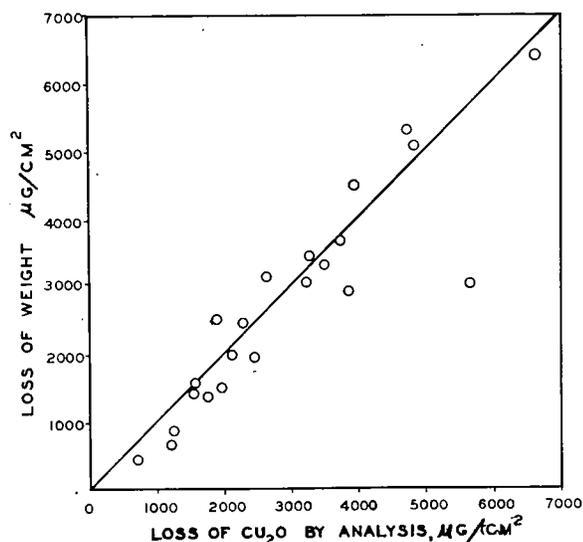


FIGURE 8. Loss in weight of Vinylite paints after 3 months' immersion in the sea, plotted against loss of cuprous oxide as determined by analysis.

traction were visibly bleached, the original bright red having paled to pink or gray, and it was clearly apparent that only a skeleton of exhausted matrix remained. In general, the higher the original proportion of toxic, the more complete the bleaching appeared to be.

(3) When such a paint is leached in the open sea for a prolonged period, there is again a close agreement between the loss in weight and the loss of cuprous oxide as determined by analysis. In Figure 8, these two quantities are plotted against each other for a series of paints compounded of

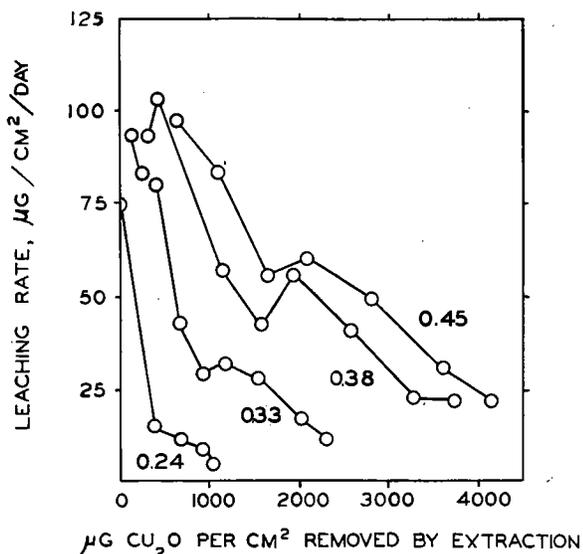


FIGURE 9. Change in leaching rate of Vinylite paints during extraction of toxic. Figures opposite curves refer to the volume fractions of cuprous oxide in the paints.

cuprous oxide, Celite, Vinylite, and rosin (18). The agreement is not quite so close as when citrated sea water is used as a solvent as in Figure 7, but it indicates clearly that only the cuprous oxide is dissolving.

(4) When the leaching rate of such a paint is measured in ordinary sea water, after various periods of extraction in citrated sea water, it is found to decrease gradually with the time of extraction (Fig. 9). The drop in leaching rate is quite slow when the original volume fraction is 0.45 (80 per cent by weight); more rapid when it is 0.33 (70 per cent by weight); and very sudden when it is 0.24 (60 per cent by weight). This be-

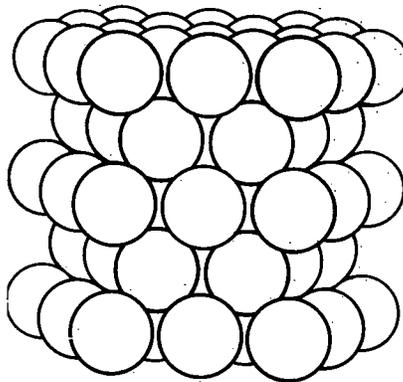


FIGURE 10. Hexagonal close packing of spheres (after W. L. Bragg, "The Crystalline State").

havior presumably reflects different degrees of perfection in the mutual contact of the toxic particles (13, 16).

To explain the concept of the degree of perfection of contact of particles, we shall consider first a hexagonal close-packed arrangement of spheres (Fig. 10). Here each particle touches twelve others and there is a complete chain of contacts throughout the structure; in other words, the mutual contact is perfect, and the probability that a given particle (for example, one on the surface) touches another is unity. In this system, the volume fraction occupied by the particles is 0.74. There are numerous other looser systems of packing spheres which afford continuous contact at lower volume fractions (25). For a cuprous-oxide Vinylite system, a volume fraction of 0.74 corresponds to 93 per cent of cuprous oxide by weight, and this should be the maximum amount that could be compounded if the particles were spherical. Actually, of course, the particles have irregular shapes and vary in size.

In practice, the proportion of cuprous oxide is never as high as 93 per cent, so that its volume

fraction is always less than 0.74. The structure is, therefore, not so closely packed as in Figure 10, and the particles may fail to make contact here and there; on the average, the probability that a given particle touches another is less than unity. If the number of particles exposed on the surface is N , and the probability that any one particle touches another is p , then the number of particles buried in the matrix which are in contact with surface particles is pN and, the number still deeper which are in contact with the latter is p^2N . In general, and speaking approximately, progressing

unity may account for limited toxic extractability and hence limited paint life, and how very small differences in this probability may result in large differences in paint behavior.

An estimate may also be made of the depth to which extraction proceeds before the leaching rate falls below the critical antifouling value of $10 \mu\text{g./cm.}^2/\text{day}$. In Figure 9 this point is reached for a toxic volume fraction of 0.45 after 4,700 $\mu\text{g./cm.}^2$ of toxic have been extracted. The number of "layers" penetrated can be found by solving the sum given in the preceding paragraph for n .

TABLE 7. Leaching Rates of Paints Containing Various Amounts of Cuprous Oxide and Celite in Vinylite

Paint Comp. Weight %			Cu ₂ O Volume Fraction	Copper Leaching Rates after Soaking ($\mu\text{g./cm.}^2/\text{day}$)					Total* Cu Leached mg./cm. ²
Vinylite	Cu ₂ O	Celite		8 wks.	12 wks.	16 wks.	20 wks.	24 wks.	
10	90	—	0.65	61	29	20	14	9	2.7
20	80	—	0.45	39	23	17	11	8	2.1
30	70	—	0.33	16	9	7	5	3	0.9
40	60	—	0.24	2	1	—	—	—	0.1
60	40	—	0.12	2	1	—	—	—	0.1
15	70	15	0.40	33	17	10	8	5	1.5
20	60	20	0.30	16	10	6	5	3	0.8
25	50	25	0.22	7	6	3	2	2	0.4

* Calculated by integration of leaching rate-time curve, assuming a linear change between each pair of measurements.

into the paint film layer by layer, at a depth of n layers of particles the number of those which touch a chain of contacts reaching the surface is Np^n . The others are isolated by being walled off by the matrix. Since p is less than unity, p^n decreases with increasing n . Thus, the deeper we progress into the paint, the fewer particles are connected by contact chains with the surface, and the more particles are isolated.

The weight of extractable toxic in n subsurface "layers" of paint, plus the surface layer, is roughly given by $d\rho v_1(1+p+p^2+\dots+p^n)$, where d is the average particle diameter, ρ the density of the toxic, and v_1 its volume fraction in the paint. The series converges for infinite n , giving $d\rho v_1/(1-p)$. It follows that only a limited amount of toxic can be dissolved from a paint with the postulated structure, no matter how long the extraction is continued. The data of Figure 9 suggest that this is indeed the case. The maximum extractable toxic may be estimated by extrapolating these data to zero leaching rate; it ranges from 1,500 $\mu\text{g./cm.}^2$ at $v_1=0.24$ to 5,000 $\mu\text{g./cm.}^2$ at $v_1=0.45$. The corresponding values of p , the contact probability, can be calculated from the above equation, taking $d=2$ microns and $\rho=6$ g./cm.³ The results are $p=0.81$ at a volume fraction of 0.24, and $p=0.89$ at a volume fraction of 0.45. This indicates how contact probabilities of only a little less than

In this case, $n=25$, so that the depth is 50 microns, or about 2 mils. According to the theory, the paint film need be no thicker than this critical extraction depth; any additional thickness is wasted.

EFFECT OF NONTOXIC PIGMENTS

The above discussion has shown that it is the volume, rather than the weight fraction, of toxic pigment which determines the value of the leaching rates of paints formulated with insoluble matrices. Additional evidence that this is the case is provided by experiments with nontoxic pigments (20).

Young, Schneider and Seagren (41) have shown that the substitution of an inert pigment for an equal weight of matrix improves the antifouling effectiveness of copper paints. The effect of substituting Celite, weight for weight, for part of the matrix of paints formulated with Vinylite and cuprous oxide is shown in Table 7. This sort of substitution increases the volume fraction occupied by the cuprous oxide in the dry film. For example, the two paints containing 70 per cent cuprous oxide by weight have cuprous oxide volume fractions of 0.33 for the paint without Celite, and of 0.40 for the paint to which Celite has been added. This results because the Celite is denser, and thus occupies less space, than the Vinylite which it replaces.

The leaching rates of the paints containing Celite are greater than those of the paints containing the same weight proportion of cuprous oxide without Celite. When compared, as in Figure 11, on the basis of the volume occupied by the cuprous oxide, however, the presence or absence of Celite appears to have a negligible effect. Additional examples which demonstrate this same effect are given in Chapter 19.

Young, Schneider, and Seagren (41) interpreted their results on the basis of an increase in the permeability of the paint. Our results, which are in agreement with theirs, can be explained as an increase in the probability of continuous contact of toxic particles, since the volume occupied by

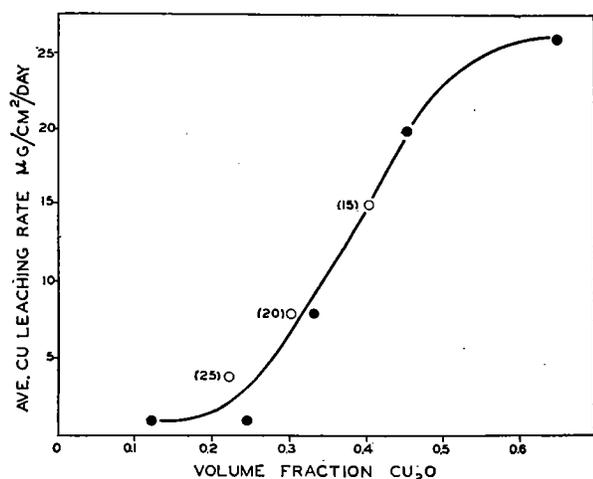


FIGURE 11. The average leaching rates related to the volume fraction of Cu₂O of Vinylite paints. O Paints containing Celite; the weight per cent of Celite is given for each paint; ● Paints containing no Celite.

the toxic in the dry paint film is increased by the substitution of the nontoxic pigment. This permits considerable latitude in developing a paint with the most effective total pigment loading, since equivalent results will be obtained if the toxic pigment volume is kept unchanged.

Table 8 shows examples of the variations in a paint formula of the composition shown in Formula A resulting from the addition of nontoxic pigment in a variety of ways. The substitution in Formula B of the nontoxic pigment for half of the matrix on an equal weight basis results in an increase of the volume fraction occupied by the toxic pigment from 0.33 to 0.39. The total pigment volume is simultaneously increased from 0.33 to 0.59. The amount by which the toxic pigment volume is increased by this addition of inerts is equivalent to increasing the weight proportion of cuprous oxide from 70 per cent to 75 per cent as

in Formula C. Conversely, if it is desired to keep the toxic pigment volume unchanged, but to increase the total pigment fraction to 0.59, as in Formula D, the weight of cuprous oxide required is reduced from 70 per cent to 63 per cent. For comparison, Formula E is given. This composition results when enough nontoxic pigment is added to the entire paint to make the total pigment volume 59 per cent. Both the weight and volume fractions of the toxic and matrix are reduced, and the resulting paint may be expected to give inadequate results.

TABLE 8. Effect of Adding an Inert Pigment (20.0 lb./gal.) in Paint Consisting only of Cuprous Oxide (48.2 lb./gal.) and Matrix (10.0 lb./gal.)

	A	B	C	D	E
Matrix wt. %	30	15	25	16	19
Cu ₂ O wt. %	70	70	75	63	46
Inert Pigment wt. %	0	15	0	21	35
Matrix vol. fraction	.67	.41	.61	.41	.41
Cu ₂ O vol. fraction	.33	.39	.39	.33	.21
Inert Pigment vol. fraction	0	.20	0	.26	.38
Total Pigment vol. fraction	.33	.59	.39	.59	.59

MECHANISMS OF CLASS TWO LEACHING

The matrix as well as the toxic may be lost from the paint, thus making available the stores of toxic in the interior of the paint film. Three possible mechanisms by which this may take place are: 1) by dissolution of the matrix, 2) by bacterial action on the matrix, and 3) by mechanical erosion of the matrix.

Some evidence that paints may lose both toxic and matrix simultaneously has been given on page 283. This was based on analyses of the dry paint film before and after a period of immersion in the sea. Additional direct evidence that steady-state leaching can progress in this way is afforded by measurements of the change in thickness of a paint film during prolonged exposure.

In one such case a formulation containing cuprous oxide, Celite, rosin, and Hercolyn was modified by the substitution of different plasticizers for the Hercolyn and by the addition of various tougheners (modifications of Navy Specification 52-P-61). When these paints were exposed at Miami Beach, Florida, the thickness was found to decrease at first, then to increase, then to decrease at a slow rate which was usually steady after three months' immersion. The copper leaching rate can be calculated from the decrease in thickness during this latter period on the assump-

tion that the loss in thickness represents a simultaneous dissolution of matrix and toxic in the proportions in which they are present in the original paint film. The leaching rates of copper were also measured directly during this period. The rates determined by these two methods are compared in Figure 12. Although the correlation is not exact, the agreement is sufficiently clear to warrant the conclusion that steady-state leaching is taking place by simultaneous removal of toxic and matrix and consequent recession of the paint surface.

Matrix Dissolution

The simplest steady-state leaching mechanism of the second class—i.e., involving removal of both toxic and matrix—is the simultaneous dissolution of both components (21). For this to be achieved, the matrix, like the toxic, must be soluble in sea water, and its rate of solution must be carefully controlled.

EVIDENCE OF MATRIX DISSOLUTION

There are several sources of evidence that this mechanism operates in many successful antifouling paints. These depend on measurements of the solubility of matrix ingredients, and on studies of extractions of paint in solutions which accelerate the dissolution of the toxic, of the matrix, or of both.

Solubilities of matrix ingredients: A common ingredient of antifouling paints is rosin, a mixture of isomeric resin acids, one of which is abietic acid, together with small amounts of neutral compounds. These acids, while insoluble in water, dissolve in alkali with formation of the corresponding salts. They have appreciable solubilities even at the very mildly alkaline reaction of sea water (pH 8.1).

Darsie (7) showed that thin rosin fibers were slowly consumed in sterile sea water, and rates of solution calculated from his measurements are of the order of $100 \mu\text{g./cm.}^2/\text{day}$. Substantial solubilities, of several hundred micrograms per cc. at the pH of sea water, have been found (35) for WW and WG rosin and for the cruder grades of K rosin, Belro resin, and Vinsol; and somewhat smaller solubilities for certain acidic rosin derivatives, such as Staybelite (a hydrogenated rosin) and Poly-Pale resin (a dimerized rosin). In the case of WW rosin and abietic acid, the solubilities were found to be proportional to the hydroxyl ion concentrations, as would be expected if a soluble salt is formed. All the neutral resins

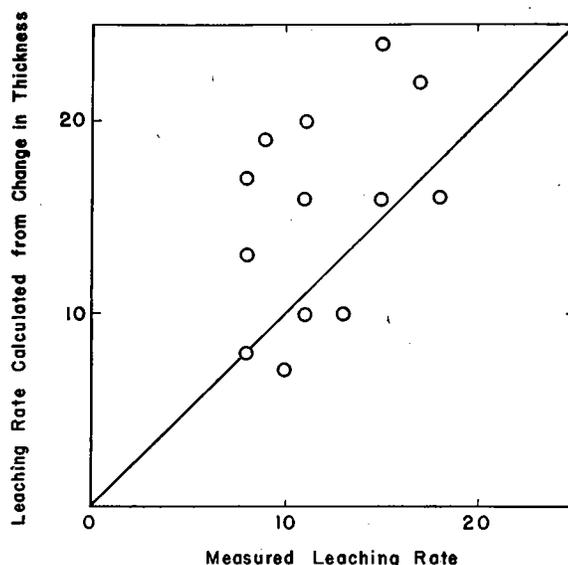


FIGURE 12. Leaching rate calculated from rate of decrease in thickness, plotted against average measured leaching rates, for modified cold plastic paints.

which have been studied, however, including ester gum (a glycerol ester of rosin), Hercolyn (a hydrogenated methyl ester of rosin), copper resin-ate, and Pentalyns M and G (modified pentaerythritol esters of rosin), have negligible solubilities at mildly alkaline reactions.

Studies of the rate of solution of matrix ingredients in sea water and in buffer solutions, described in Chapter 17, have afforded the following information on matrix dissolution:

1. The rosin dissolved from a coated panel agitated in sea water is of the order of several hundred micrograms per square centimeter over a 24-hour period. The rate of solution is not constant, however, but gradually decreases with time.

2. The rate of solution of rosin increases with preliminary aging of the film in air, owing presumably to oxidation with the formation of more highly soluble products.

3. The presence of calcium and magnesium ions in buffer solutions, and in sea water, decreases the rate of solution of rosin, owing presumably to chemical combination.

4. The rate of solution of an acidic resin is decreased by the incorporation of neutral resin. Complicated phase relationships in mixtures make it necessary to study each binary system individually to determine the dependence of solution rate on composition.

It was also found that the matrices of certain antifouling paints, compounded with all ingredients present except the pigments, dissolved in sea water at measurable rates. For example, the

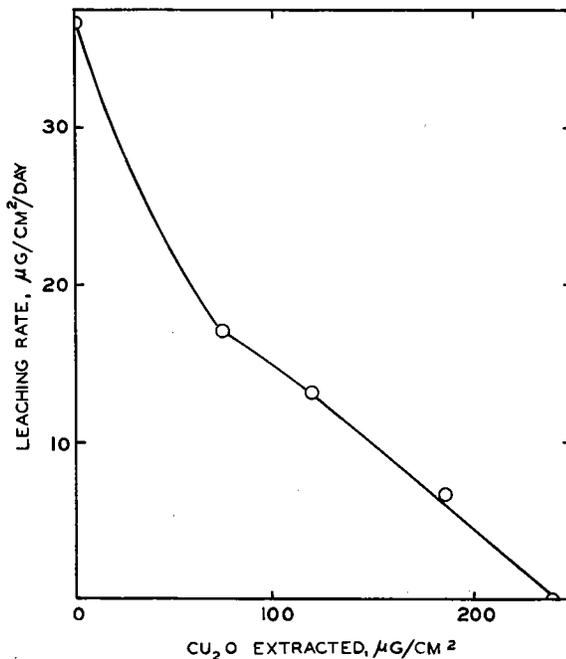


FIGURE 13. Surface exhaustion of cold plastic paint (143E) by extraction in sea water acidified to pH 4.

matrix of the cold plastic paint 143E dissolved in running sea water at a rate of about $100 \mu\text{g./cm.}^2/\text{day}$ (14).

Successive extractions of paint in acid and in sea water: Having cited the evidence that certain ingredients of paint matrices are soluble, we shall now describe experiments which indicate how this is related to the maintenance of steady-state leaching.

Panels coated with the cold plastic paint 143E were treated with sea water acidified to pH 4 with hydrochloric acid. Under this condition, the surface-exposed cuprous oxide is rapidly dissolved, whereas the solubility of the acidic matrix components is negligible. Accordingly, surface exhaustion of the toxic takes place, just as in the

TABLE 9. Recovery of the Steady State Leaching Rate of Paint 143E After the Removal of Various Amounts of Surface Toxic in Sea Water Acidified to pH 4

Days in Sea Water at pH 4	Cu ₂ O Removed μg./cm. ²	Leaching Rate, μg./cm. ² /day, After Soaking in Sea Water for		
		1 hr. ^a	4 hr. ^b	24 hr. ^c
1	41	2.2	4.7	14.1
2	64	4.9	8.9	14.5
3	74	2.5	8.1	12.5
4	83	4.0	5.6	12.7
5	116	1.7	3.4	
7	153	0	2.0	11.5
8	172	1.7	2.2	10.8
9	172	0	2.7	12.0

^a Calculated on the basis of 1 hour leaching.

^b Calculated on the basis of 4 hours' leaching.

^c Running sea water; calculated on the basis of 4 hours' leaching.

insoluble Vinylite paints described on page 280. Leaching rates, measured in ordinary sea water after varying periods of acid extraction, are plotted against the amount of toxic removed, in Figure 13. The resulting curve is similar to those which describe the surface exhaustion of Vinylite paints in sea water (Fig. 5). The leaching rate becomes zero after $240 \mu\text{g.}$ cuprous oxide per sq. cm. have been removed. This is the right order of magnitude for the quantity of surface-exposed toxic on a freshly-painted surface. Clearly, only the surface toxic has been dissolved, and the mechanism which normally operates in the sea to maintain leaching from the interior of the paint film has not functioned in the acidified solution.

However, after the surface toxic has been exhausted, the ability of this paint to leach at an adequate rate can be rapidly restored by soaking in sea water. Panels which had been leached in the acid sea water (pH 4) were rinsed and returned to normal sea water, and the leaching rates measured after various times. The results of this experiment are given in Table 9. The leaching rates of all of the panels increased during the first four hours of soaking in sea water, and all had reached values between 10.8 and $14.5 \mu\text{g./cm.}^2/\text{day}$ by the end of 24 hours in sea water.

It is apparent that the exhausted surface has been regenerated by sea water soaking; a new layer of cuprous oxide particles has presumably been uncovered by removing the layer of matrix which remained after the acid treatment. The removal might be attributed either to the solvent action of sea water or to its erosive action in flowing past the surface. Actually, experiments on erosion, described below, indicate that mechanical action is of minor importance, while the significance of dissolution is shown by the following experiments on regeneration in alkaline solution.

Successive extractions of paint in acid sea water and in alkaline tap water: In a procedure developed by the Mare Island investigators (26), freshly painted panels are first extracted in acidified sea water as described above, and then in tap water adjusted with sodium hydroxide to pH 11.5, the leaching rate being measured after each extraction. The acid treatment is carried out for 3 days, in 3 successive changes of solvent, and results in a marked diminution of the leaching rate, attributable to surface exhaustion. The alkaline treatment is carried out for only 3 hours, and results in a substantial increase in the leaching rate (Tables 10 and 11). Evidently a new layer of cuprous oxide particles is uncovered by removal of matrix; the

rapid regeneration produced by raising the pH of the solvent indicates that the process is one of matrix dissolution.

It is significant that most of those paint formulations which do not maintain adequate steady-state leaching rates in service and do not satisfactorily prevent fouling are not regenerated by the alkaline treatment described above. Such unsatisfactory paints, once exhausted of surface toxic, retain their low leaching rates after extraction in alkaline tap water. The correlation between alkaline regeneration and the ability to maintain steady-state leaching in service, as found in the studies of the Mare Island Paint Laboratory, is further evidence that steady-state leaching, in those paints in which both toxic and matrix are lost, depends primarily upon the solubility of the matrix in a slightly basic solution.

Extractions of paint in glycine: The Mare Island toxic regeneration test described above depends upon two successive extractions: first, of toxic, under conditions where the solubility of toxic is enhanced and that of the matrix suppressed; and, second, of matrix, under conditions where the solubility of the matrix is enhanced and that of the toxic suppressed. It is also possible to extract a paint under conditions where the solubilities of both phases of the paint are high. Alkaline solutions of sodium glycinate and sodium chloride serve this purpose (19, 23). The resin acids are held in solution by the alkaline buffer and the copper is dissolved as a cupric glycinate complex ion. In such a solvent (0.025 M sodium glycinate, 0.48 sodium chloride, pH 10.5), paints dissolve approximately a hundred times as fast as in steady-state leaching in the sea, until several thousand micrograms of cuprous oxide per square centimeter have been removed. The leaching thus extends deep into the body of the paint. When the glycine extract is acidified and extracted with ether, substantial quantities of resins are recovered, showing that the matrix has dissolved along with the toxic as the leaching proceeds. Some examples of the amounts of toxic and matrix dissolved by this procedure are shown in Table 12. The figures show that substantial thicknesses of paint, many times the diameter of a toxic particle, have been removed by the treatment. The proportion of cuprous oxide to acid resin dissolved is close to their original proportion in the paint, indicating simultaneous dissolution.

Just as in the case of the alkaline regeneration test, there is a correlation with paint performance in service; most paints which do not maintain

TABLE 10. Recovery of Leaching Rate of Surface-Exhausted Paint by Extraction in Alkaline Tap Water

Paint	Leaching Rate in Sea Water, $\mu\text{g./cm.}^2/\text{day}^a$		
	Initial ^b	After Acid Treatment	After Alkaline Treatment
143E	40	1.5	24.0
42-3	40	2.5	47.5
42-3A	38	1.5	22.2
16X	30	14.7	24.5

^a Agitation by standard bubbling.

^b Representative values from measurements on other panels.

TABLE 11. Recovery of Leaching Rate of Surface-Exhausted Paint by Extraction in Alkaline Tap Water

Paint	$\mu\text{g. Cu per cc. Dissolved in 2 Hours}^a$	
	After Acid Treatment	After Alkaline Treatment
143E	0.2	1.2
142D	0.2	0.8
145	0.2	1.0
16X	0.5	1.5

^a Agitation by rotation of panel at 100 r.p.m.

adequate steady-state leaching rates in service do not undergo rapid dissolution in the glycine buffer. The utility of the glycine solution in accelerated testing procedures is discussed in Chapter 20. It suffices here to point out that the correlation between rate of solution in alkaline glycine and maintenance of steady-state leaching in the sea affords further excellent evidence that the latter phenomenon depends upon the solubility of the matrix in a slightly alkaline solution.

To sum up, we have the following evidence that many antifouling paints of Class Two, which, as shown in Table 4, lose toxic and matrix simultaneously in the same proportions in which they are originally compounded, maintain steady-state leaching rates by dissolution of the matrix: (1) the acidic ingredients which are present in most antifouling paint matrices have substantial solubilities in sea water, and the matrices themselves can dissolve at rates which are of the order of magnitude of leaching rates; (2) the mechanism which maintains steady-state leaching in normal sea water does not operate in acidified sea water,

TABLE 12. Dissolution of Both Toxic and Matrix in Alkaline Glycine Solutions (3 Days in 0.025 M Sodium Glycinate, 0.48 M Sodium Chloride, pH 10.5)

Paint	Ratio of Cuprous Oxide to Rosin in Paint	Amounts Dissolved, $\mu\text{g./cm.}^2$		Ratio
		Copper as Cu_2O	Acid Resins	
143 ^a	1.20	4,480	3,710	1.21
16X ^a	2.00	4,500	2,370	1.90
WG ^b	2.50	3,160	1,460	2.16
E ^b	2.50	4,600	1,970	2.34

^a Averages of five determinations.

^b Averages of four determinations.

but is restored after the paint is returned to normal sea water, and is rapidly regained by treatment with a dilute alkaline solution; (3) the entire process of steady-state leaching is enormously accelerated in an alkaline solution of glycine, in which the amounts of copper and acid resin dissolved are roughly in the same proportions as those in the paint; (4) neither the regeneration in dilute alkaline solution nor the acceleration in alkaline glycine solution is operative for most paints which do not in practice maintain adequate steady-state leaching rates in service.

SIMPLIFIED THEORY OF STEADY-STATE LEACHING BY MATRIX DISSOLUTION

If a steady-state of leaching is attained in which the dissolution of toxic and the dissolution of

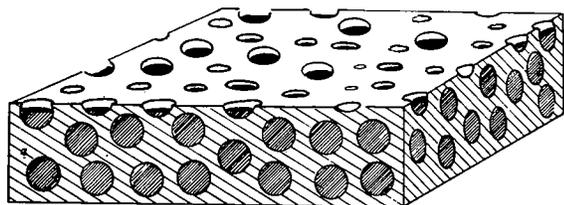


FIGURE 14. Schematic diagram of steady-state leaching by matrix dissolution

matrix keep pace with each other, the rates at which they are lost from the paint must be proportional to their weight fractions in the mixture; thus the following equation must be fulfilled:

$$L_1/L_2 = w_1/w_2 \quad (2)$$

where L_1 and L_2 are the leaching rates of toxic and matrix, respectively, and w_1 and w_2 are their weight fractions in the paint.¹ This equation is independent of any assumptions concerning the mechanism of dissolution or the geometrical details of the simultaneous exposure of both toxic and matrix.

Now, each leaching rate is a product of an intrinsic rate of solution and the ratio of the area exposed to the area considered as a plane. Thus, as previously stated in equation (1),

$$L_1 = k \frac{a}{A} \quad (1)$$

where k is the intrinsic rate of solution of cuprous oxide and a is the actual area of toxic exposed on a paint surface of area A (considered as a plane). Similarly, for the matrix,

¹ If the toxic is cuprous oxide, L_1 is expressed in terms of cuprous oxide, not copper.

$$L_2 = R_2 \frac{a_2}{A} \quad (3)$$

where R_2 is the intrinsic rate of solution of the matrix, and a_2 is the area exposed. The meaning of these areas may be clarified by reference to Figure 14.

If the assumption be made that toxic particles are disposed randomly, as shown in Figure 14, and the matrix surface is a plane intersecting them, then a_2/A (neglecting exposed matrix in the pits) is calculated to be equal to v_2 , the volume fraction of matrix.² By combining with equations (2) and (3), we obtain

$$L_1 = w_1 R_2 v_2 / w_2 \quad (4)$$

which is a theoretical expression for the steady-state leaching rate controlled entirely by matrix dissolution.

The intrinsic rate of solution of the toxic does not enter into this expression. Qualitatively, this result would be expected when the matrix dissolves much more slowly than the toxic, and therefore solely determines the over-all solution rate. In the hypothetical case of an insoluble "toxic," the scheme on which equation (4) is derived provides for the undermining of the toxic particles, which then drop off as the matrix recedes. In this case, equation (2) would still be fulfilled, but the "toxic" would not pass into solution and therefore would not contribute to antifouling action.

Equation (4) is based on an oversimplification of steady-state leaching and neglects several complicating factors which will be introduced later. However, it is useful for illustrating the principles of simultaneous dissolution.

Evaluation of the intrinsic rate of solution of matrix from toxic leaching rate data: If the steady-state toxic leaching rate and the paint composition are known, then the intrinsic rate of solution of the matrix under steady-state conditions can be calculated from equation (4). For example, Table 13 gives these data for a series of cold plastic paints containing different amounts of cuprous oxide made up in the same matrix, the pigment volume fraction being kept constant at 0.12 by replacing cuprous oxide by magnesium silicate. The calculated values for the intrinsic leaching rate of the matrix are about 40 $\mu\text{g./cm.}^2/\text{day}$, which is certainly the right order of magnitude, a value of

² The exposed matrix area is taken as the area, A , of the plane surface in Figure 14, minus the circles cut out by intersections with toxic particles. The sum of the latter areas, assuming random distribution of particles (N per unit volume), is

$$\pi N A \int_0^{2r} (2rz - z^2) dz = \frac{4}{3} \pi r^3 N A = v_1 A.$$

The matrix area is, therefore, $a_2 = A - v_1 A = v_2 A$.

TABLE 13. Steady-State Leaching Rates of Cold Plastic Paints

Paint No.	w_1	w_2	Average	R_2 , Calc.
			Leaching Rate $\mu\text{g./cm.}^2/\text{day}$ 2-5 mos.	
4	0.04	0.74	2.2	46
5	0.08	0.72	4.3	44
6	0.14	0.70	6.9	39
7	0.20	0.68	9.2	36
8	0.24	0.66	11.3	35
9	0.30	0.64	12.7	31

about 100 having been obtained for the pure matrix (page 289). However, the fact that R_2 is not constant for the entire series indicates that the oversimplified theory is not strictly applicable.

Estimation of requisite matrix dissolution rates: From equation (4), an indication may be obtained of the matrix dissolution rate which is required to maintain an adequate toxic leaching rate in a paint of given composition. For example, in a cuprous oxide paint, in a matrix whose density is 1.25, the intrinsic matrix solution rates required to maintain a toxic leaching rate of 10 are given in Table 14 for various toxic loadings. The required value decreases rapidly with increase in loading and becomes very small as the proportion of cuprous oxide approaches that required for continuous contact (page 285). The table also shows that the weight of paint per unit area, and the thickness, required for a life of one year decrease rapidly with increasing loading with cuprous oxide.

Several other relationships follow from the oversimplified equation (4) and are worth pointing out:

(1) For constant loading, the leaching rate is directly proportional to the intrinsic solution rate of the matrix.

(2) If the utilization efficiency of the paint be defined as the ratio of the minimum effective leaching rate ($10 \mu\text{g./cm.}^2/\text{day}$) to the actual leaching rate, then this efficiency is inversely proportional to the intrinsic solution rate of the matrix.

(3) The thickness of paint film required for a given life, e.g., one year, is directly proportional to the intrinsic solution rate and is independent of the proportion of toxic present. When the toxic loading is high, more toxic is wasted, to be sure, and a greater weight per unit area must be applied; but owing to the higher density of the toxic, the thickness of the film is exactly the same as for low loadings.

It is clear from these relationships that the adjustment of the intrinsic solution rate of the matrix is of the greatest importance in compounding an antifouling paint which is effective and yet does not waste too much toxic.

With this background of simplified theory for

TABLE 14. Intrinsic Matrix Dissolution Rates Required to Maintain a Copper Leaching Rate of $10 \mu\text{g./cm.}^2/\text{day}$, Calculated from Equation (4)

Weight per cent of Cuprous Oxide	Matrix Solution Rate Required	Weight per Unit Area Required for Life of 1 Year, $\mu\text{g./cm.}^2$	Thickness Required for Life of 1 Year, mil
10	92	36,000	10
20	42	18,000	5
30	25	12,000	3
40	17	9,000	2
50	12	7,000	1
60	9	6,000	1
70	6	5,000	1

simultaneous dissolution of toxic and matrix, we shall now proceed to a description of further experiments which require a somewhat more complicated interpretation.

MEASUREMENTS OF SIMULTANEOUS LOSSES OF TOXIC AND MATRIX IN STEADY-STATE LEACHING

The dissolution of toxic and of matrix during immersion of an antifouling paint in the sea for a prolonged period can be followed by total analysis of the paint film, sampled at different intervals. Examples of this type of experiment have already been given on page 282, to show the contrast between the two general classes of steady-state leaching mechanisms. Further studies are now described to show in how far the simplified theory of matrix dissolution is applicable to actual paint systems. The loss of matrix is, as before, taken as the difference between the total loss of weight and the loss of toxic.

If equation (4) is fulfilled at all times, even though the leaching rates of both toxic and matrix may change with time, over the time interval Δt the following relation should hold:

$$(\Delta T/\Delta t)/w_1 = (\Delta M/\Delta t)/w_2 \quad (5)$$

where ΔT and ΔM are the quantities of toxic and matrix, respectively, dissolved during the interval Δt .

Results for a series of paints made up with cuprous oxide, rosin, and various amounts of different neutral resins (Hercolyn, ester gum, and copper resinate) are given in Table 15. Here values of $(\Delta T/\Delta t)/w_1$ and $(\Delta M/\Delta t)/w_2$ have been calculated for the period from the fourth to the eighth or twelfth week of immersion in the sea.

In every case, the value of $(\Delta T/\Delta t)/w_1$ is greater than that of $(\Delta M/\Delta t)/w_2$, showing that toxic has been lost in excess of its proportion in the paint. In fact, in several cases there has actually been a gain in the weight of matrix over the interval specified. There are two possible interpretations for this phenomenon. First, chemical reaction of

the matrix or toxic with sea water may form a deposit on the paint surface whose additional weight causes the figure for matrix loss to appear too small. Second, the soluble components of the matrix (acid resins) may dissolve out, leaving an accumulation of the insoluble components on the paint surface.

Both of these two possible effects may occur. Their respective contributions cannot be distinguished without further analysis, but the total weight per unit area of matrix and/or deposit accumulation can be calculated and is given in the table. It is of considerable magnitude, often

the dissolution underneath. The lag between dissolution of the soluble and erosion of the insoluble ingredients should depend upon the mechanical characteristics of the latter.

Actually, both these effects are clearly evident in the behavior of matrix films in the absence of toxics (Chapter 17). The calcium and magnesium in sea water combine with acidic resins to form surface deposits which depress the rate of solution. In a mixture of acidic with neutral resins, the rate of solution of the acidic resin is lowered, to an extent which appears to depend on the mechanical properties of the neutral component—the higher

TABLE 15. Simultaneous Loss of Toxic and Matrix

Neutral Resin Added	% Total Neutral Resin*	Interval of Immersion, weeks	$\frac{\Delta T}{\Delta t}$	$\frac{\Delta M}{\Delta t}$	Matrix Accumulation $\mu\text{g./cm.}^2$	Total Weight Lost $\mu\text{g./cm.}^2$
			w_1	w_2		
Ester Gum	25	4-8	45	32	230	1,030
	30	4-8	24	-4**	500	170
Copper Resinate	14	4-8	70	36	610	1,371
	18	4-8	114	60	970	2,220
Hercolyn	13	4-12	20	6	500	615
	18	4-12	25	12	470	935
	24	4-12	17	-3**	720	228
	29	4-12	8	-1**	320	126
	36	4-12	15	6	750	516

* Including neutral material present in the resin.

** Apparent gain in matrix.

exceeding the total loss in weight during the interval of immersion.

Many other measurements of this sort have shown that, in the simultaneous dissolution of toxic and matrix, the amount of dissolved matrix as calculated by difference is almost always less than specified by the simple theoretical relation of equation (2).

FACTORS MODIFYING^o THE SIMPLIFIED THEORY

If an insoluble deposit is formed on the paint surface as a result of reaction of sea salts with certain ingredients of either toxic or matrix phases, the rates of solution of both toxic and matrix may be slowed down. In the end, a steady-state may be achieved in which the leaching rate is determined by the rates of formation of deposit and of its removal by erosion, as well as by the rate of solution of the matrix.

Similarly, if a portion of the matrix is insoluble and is left behind as a surface accumulation after the soluble matrix components have dissolved away, this accumulation will impede the dissolution of both the toxic and the soluble part of the matrix. The depth of surface accumulation would be expected to increase with time, but in the end a steady state might be reached in which erosion of the insoluble material would keep pace with

its viscosity, the greater its impeding effect.

It is not possible at present to make any quantitative theoretical description of the effects of surface deposits or accumulation of insoluble matrix materials on steady-state leaching. However, in a qualitative way, studies of these phenomena with films of pure matrix, as described in Chapter 17, can be applied to the interpretation of the more complicated paint systems which contain both matrix and toxic.

The initial anomalies in leaching for which the toxic is responsible are eliminated within a few days after immersion in the sea, since the toxic originally exposed on the surface is dissolved within this period. In practice, however, the leaching rate of a paint may undergo considerable change for a period of several weeks, before settling down to a relatively constant value. These changes are attributable to the matrix, and probably represent the approach to a steady state with respect to deposit formation and surface accumulation of insoluble matrix ingredients.

Bacterial Attack of Matrices

Another possible mechanism for gradual removal of the matrix of an antifouling paint to permit prolonged steady-state leaching is bacterial decomposition.

When a surface is first exposed in the sea, a slime film begins to form. This is composed of bacteria and diatoms together with certain sticky metabolic products to which adhere various amounts of organic and inorganic detritus. The possible role of the slime film in preventing the attachment of fouling has been discussed in Chapter 14, where it was concluded that the most important property of the slime in this connection is its toxic content. Copper leached from a paint combines with the organic matter of the slime (11, 36), and may also be precipitated in the slime as the relatively insoluble basic cupric carbonate.

Because of the chemical affinity of the slime film for copper, its presence might be expected to diminish the leaching rate; accumulation of copper by the slime would reduce the total amount escaping to the surrounding sea water. The magnitude of such an effect can be estimated by comparing the leaching rate of a slime-coated panel with its leaching rate after the slime has been carefully scraped off. Whedon and his collaborators (39) have studied a large number of paints in this way. In a majority of cases the removal of the slime resulted in a slight increase in the leaching rate (Table 16). Also, experiments by Riley (31) showed that, for paints containing mercury as the toxic, removal of the slime invariably resulted in a slightly increased leaching rate.

Experiments such as these show the effect of the slime film on the leaching rate at the time the measurement is made, but give no information concerning the contribution of bacterial action to the maintenance of steady-state leaching. The possibility that the bacterial population of the slime film can so contribute is inherent in the fact that many matrix ingredients, such as rosin,

paraffin, and copper resinate, can be decomposed by marine bacteria (7, 30).

In an attempt to evaluate the role of bacterial action, Renn and Johnstone (30) partially inhibited the development of bacterial slimes on antifouling paints by periodically immersing each panel in a bactericidal solution of sodium pentachlorophenate during the course of steady-state leaching. The steady-state leaching rates of these panels were compared with those of control panels on which the bacterial slime was allowed to grow (Table 17).

TABLE 17. Effect of Periodic Disinfection on the Leaching Rates of Various Paints

Paint	Time of Immersion, Weeks	Copper Leaching Rates μg./cm. ² /day	
		Untreated	Disinfected
142C	4	7.4	4.1
142C	7	7.3	4.7
143E	4	14.4	8.4
1B8	4	2.9	2.2
16X	4	28.0	42.0
AF6	4	22.0	31.0

For the first three paints in the table, all of which contain rosin, the untreated panels gave higher leaching rates than did the disinfected panels, indicating that bacterial activity was contributing to the release of toxic. However, for paint 1B8, which contained ester gum, the difference was slight, and for 16X (rosin and Herculyn) and AF6 (rosin and Vinylite) the disinfected panels had higher leaching rates than the controls—a result which is difficult to interpret.

These investigations indicate that bacterial action may have sufficient influence on an antifouling paint film to require its consideration in theoretical studies. However, the paints upon which the bacterial action has been shown to have a significant effect have matrices which are sufficiently soluble to ensure effective leaching without the action of bacteria. It seems probable that under normal conditions of service, bacterial action is inadequate to insure the success of a formulation through maintenance of steady-state leaching by this mechanism alone.

In any case, it is certain that very little can be done by the paint technologist in order to stimulate or control bacterial decomposition of a paint matrix. The bacterial film forms on practically any surface exposed to the sea. It is true that the growth is somewhat heavier on paints containing rosin and similar materials which contribute to the nutrition of the organisms; and it is somewhat lighter on surfaces with high copper leaching rates such as panels of copper metal or heavily loaded cuprous oxide paints. However, the pros-

TABLE 16. Copper Leaching Rates of Various Painted Panels with the Slime Film Intact and After the Removal of the Slime

Paint	% Cu ₂ O in Paint ^a	Time of Immersion, Weeks	Leaching Rate μg./cm. ² /day		Conc. Cu in Slime ^b
			With Slime	De-slimed	
10C	40	4	18.9	29.7	6.73
9C	30	4	19.7	29.2	6.40
7C	20	4	14.6	16.8	6.39
5C	10	4	4.2	3.6	1.44
10C	40	10	14.3	14.1	10.1
9C	30	10	14.1	13.2	10.8
7C	20	10	14.1	13.0	6.50
5C	10	10	3.5	3.8	3.29
42-3Ax	38	4	24.9	26.0	2.92
42-3A	30	4	16.4	20.5	2.95
42-3Aa	23	4	16.3	16.7	2.45
42-3Ab	15	4	10.8	10.8	1.88
			3.2	3.1	0.44
42-3Ac	8	4	6.2	5.7	0.63

^a Values calculated from paint formulation.

^b Values given in per cent of organic matter.

pect of maintaining steady-state leaching rates by controlling the intensity of bacterial metabolism does not appear to be a promising one.

Mechanical Erosion of Matrices

Erosion is another mechanism which may maintain steady-state leaching by gradual removal of

TABLE 18. Effect of Mechanical Wear upon Matrix Erosion, Panels Rotated at 1,500 R.P.M.

Paint	Antifouling Performance	$\mu\text{g. Cu per cc. Dissolved in 2 Hours}^a$		
		After Acid Treatment	After 8 hrs. Wear	After 20 hrs. Wear
42-3	Excellent	0.10	0.13	0.10
42-4	Poor	0.15	0.13	0.13
143E	Excellent	0.15	0.14	0.16
1-B-10	Very Poor	0.30	0.10	0.09

^a Agitation for leaching by rotation of panel at 100 r.p.m.

TABLE 19. Effect of Wet Abrasion^a upon Matrix Erosion

Paint	Antifouling Performance	$\mu\text{g. Cu per cc. Dissolved in 2 Hours}^b$		
		After Acid Treatment	After 50 Strokes	After 150 Strokes
3Z	Excellent	0.35	0.32	0.22
4Z	Very Poor	0.10	0.07	0.11
13Z	Very Poor	0.10	0.07	0.09
16Z	Very Poor	0.10	0.07	0.11

^a Federal Specification TT-P-88.

^b Agitation for leaching by rotation of panel at 100 r.p.m.

TABLE 20. Decrease in Thickness of Paint 143E During Mechanical Wear, Panels Rotated at 750 R.P.M. 21 Days

No. of Coats	Drying Time, hrs.	Decrease in Thickness from 7th to 21st Day, mils		
		Radius 1-1.5" 8 ft./sec.	Radius 3-4.5" 25 ft./sec.	Radius 5-6.5" 38 ft./sec.
1	24	2.0	2.2	2.5
1	72	1.0	0.5	0.5
3	40	2.3	3.0	3.2
3	168	1.0	0	1.5

matrix. It differs from dissolution primarily in that the particles which become detached are of greater size than the molecules set free in dissolution. Mechanical forces associated with friction are commonly considered to be responsible for breaking free the eroding particles. Chemical action must frequently facilitate erosion by disintegrating the structure of the paint surface and thus permitting small particles to become detached more readily.

The loss of particles of paint has also been considered as a possible mechanism for the prevention of fouling by exfoliation (Chapter 13). We are concerned here solely with the role of erosion in maintaining steady-state toxic leaching rates by uncovering the deeper stores of toxic particles.

In an attempt to appraise the importance of erosion of the matrix in uncovering fresh layers of toxic from the interior of paints, the Mare Island investigators extracted the toxic from the surface of typical hot and cold plastic paints and then examined the effects of rather drastic erosive treatments (26). The surface-exposed cuprous oxide was extracted in sea water acidified to pH 4 (cf. p. 290). Leaching rate determinations after four days in this solution showed that the surface had been almost exhausted of toxic. The panels were then bolted on a special jig and rotated at approximately 1,500 r.p.m. in sea water. The velocity of the panel surface was approximately 45 feet per second, but the velocity relative to sea water was somewhat less than this, owing to swirling in the un baffled container. After eight hours of this treatment, leaching rates were again determined, and were repeated after an additional twelve hours. Very little increase in the leaching rate was observed (Table 18). Additional tests (26) conducted by these investigators included the use of a wet abrasion apparatus,¹ which also resulted in no significant increase in the leaching rate (Table 19). The results indicate that for these paints, at least, erosion was not effective in uncovering a fresh layer of toxic particles.

On the other hand, measurements at Miami of the change in thickness of paint 143E under somewhat similar conditions of high surface velocity show that the rate of loss was considerably higher than that calculated from the leaching rate under laboratory conditions (37). Painted discs were rotated at 750 r.p.m. for 21 days in sea water. The thickness measurements are complicated by the swelling of the paint film (cf. p. 288); to minimize such complications, the change in thickness from the seventh to the twenty-first day of rotation was taken for comparison. At various distances from the center of rotation, corresponding to various surface velocities, the decrease in thickness ranged from 1 to 3 mils (Table 20). By contrast, the value calculated on the basis of a leaching rate of $15 \mu\text{g./cm.}^2/\text{day}$ is only 0.1 mil. Thus a considerable acceleration of paint loss, attributable to erosion, was indicated.

Some of the soft commercial paints undoubtedly erode to considerable extents in active service. Most paint films suffer gross failure under extreme conditions of friction, as evidenced by flow in the surface layers or by stripping away from the substrate (32, 33, 34). However, up to the point where these visible signs of failure are present, the role

¹ Federal Specification TT-P-88.

of erosion in antifouling paint performance remains questionable. In any case, like bacterial action, erosion does not seem to be a mechanism for steady-state leaching which is readily susceptible to control by the paint technologist.

Depression of Leaching by the Formation of Deposits

The most important reactions which occur at the surface of an antifouling paint in sea water are those which lead to the formation of soluble products, and it is upon these reactions that the maintenance of steady-state leaching depends. The formation of soluble compounds from the toxic phase has been discussed in Chapter 15, and the formation of soluble compounds from the matrix phase will be further discussed in Chapter 17.

Side reactions may lead to the formation of insoluble compounds, which may adhere to the paint surface and depress its leaching rate. As examples of insoluble compounds formed from the toxic, basic cupric carbonate and chloride are often deposited on paints containing cuprous oxide or metallic copper. As examples of compounds formed from the matrix, the calcium and magnesium salts of rosin may be cited. A third possible type of deposit may consist of sea salts, precipitated upon a substrate without actually reacting with it, as in the case of the deposits formed in the presence of electric fields described in Chapter 13. Although knowledge of these different types of deposits is very incomplete, it will be summarized in its present state.

Evidence for deposit formation from changes in composition during soaking: Analysis of the changes in composition and weight of an antifouling paint during soaking afford an opportunity for calculating the apparent losses of toxic and matrix from the paint. It has already been shown in Table 15 that in some experiments of this sort an apparent *gain* in the weight of matrix is found. Table 21 cites some still more striking examples, in which, despite substantial losses of toxic, the total change in the weight of the paint may be

practically zero and the apparent gain in matrix balances the loss of toxic. In such cases there appears to be little doubt that material has been deposited from the sea water.

Evidence for deposit formation from inspection: Several investigators (38) have noticed that films of cuprous oxide paints, after immersion in the sea, develop a green coloration on the surface which is probably a deposit of basic cupric carbonate and/or cupric oxychloride. From the sequence of reactions in the dissolution of cuprous oxide in sea water, as outlined in Chapter 15, it is to be expected that those paints with the highest leaching rates should show the greatest tendency for cupric salts to precipitate in the vicinity of the paint surface. The factors which determine whether the precipitated cupric salts adhere firmly to the surface are not, however, understood.

Since the cupric salts have much lower solubilities than that of cuprous oxide, it is to be expected that any covering of cuprous oxide by such a deposit would decrease the leaching rate of the paint. The following experiments demonstrate this effect.

Evidence for deposit formation from changes in leaching rate during soaking: When a Vinylite paint with very high cuprous oxide content is subjected to prolonged extraction, the leaching rate measured in ordinary sea water gradually falls, whether the extraction takes place in citrated sea water (Fig. 9) or in the sea (Fig. 3a). This behavior has been attributed to imperfections in the chains of continuous contact between particles; the degree of imperfection becomes progressively worse as the extraction proceeds deeper into the paint film, and the leaching rate consequently falls (page 286). Any formation of a deposit of cupric salts of low solubility should further depress the leaching rate. This effect should appear only in the sea, and not in citrated sea water, since the citrate forms a highly soluble cupric complex and prevents precipitation of cupric copper (Chapter 15). Thus, the effect of a deposit can be assessed by comparing the leaching rates, in sea water, of a paint which has been extracted in citrate solutions and in the sea.

Figure 15 shows leaching rates in sea water of a paint after the extraction of various amounts of cuprous oxide in citrated solutions and in the sea. The amount of toxic dissolved in the sea is calculated by integrating the curves of leaching rate against time. The leaching rates, which are determined in the laboratory, must be corrected to the prevailing temperature of the sea by a

TABLE 21. Losses and Gains in Weight of Paints after Immersion in the Sea

Paint	Time of Immersion	Change in Weight, $\mu\text{g./cm.}^2$		
		Total	Cu_2O	Matrix*
1B7**	1 month	-270	-460	+190
	2 months	-360	-746	+386
1B11#	1 month	0	-540	+540
	2 months	+63	-1,178	+1,241

* By difference.

** Cuprous oxide, ester gum, Herculyn, Dicalite.

Cuprous oxide, "Cumar" P-10, Herculyn, Dicalite.

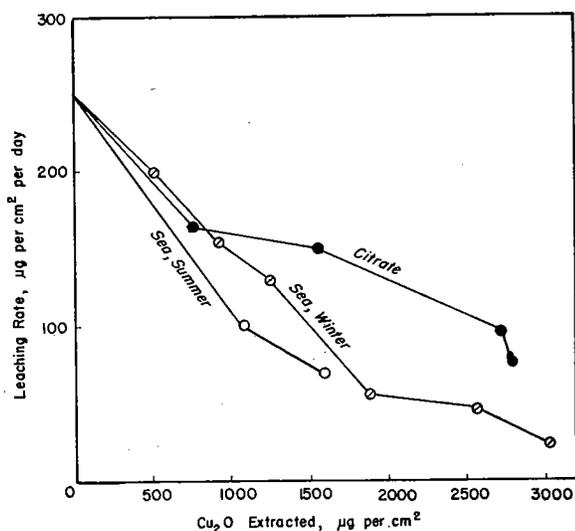


FIGURE 15. Leaching rate in normal sea water of a paint consisting of 90 per cent cuprous oxide and 10 per cent Vinylite, plotted against the amount of toxic extracted in citrate sea water and in the sea in winter and summer.

temperature correction factor (12). The curves for sea extraction in summer (average temperature 23.5°C.) and in winter (average temperature 1.5°C.) lie close together. After 1,500 $\mu\text{g./cm.}^2$ of cuprous oxide had been extracted from the sea-extracted panels, they developed a greenish color, indicating the formation of a deposit of cupric salts. The curve for extraction in citrate coincides with the other curves up to extraction of about 1,000 $\mu\text{g.}$ of toxic per sq. cm., but thereafter falls much more slowly. The citrate-extracted panels in this experiment retained their red color and showed no evidence of deposit formation.

The results in citrate presumably represent the geometrical effect of incomplete continuous contact, while the difference between the results in citrate and in the sea represents the effect of a deposit.

Composition of deposits: There are no data available on the chemical composition of deposits formed on the surfaces of antifouling paints. In so far as they are composed of basic cupric carbonate, they may be expected to contribute to the copper leaching rate to some extent, although much less than an equivalent surface of cuprous oxide. Deposits of cupric oxychloride, however, which apparently has a very low solubility, or of calcareous precipitates of sea salts, as suggested by Copisarow (6), may be expected to be inert and to impede the process of leaching.

Fundamental Principles in the Design of Antifouling Paints

Of the five possible mechanisms for maintaining steady-state leaching which have been discussed,

there are only two which are in practice widely utilized: continuous contact of toxic particles, and matrix dissolution. Most successful antifouling paints operate through one or the other of these mechanisms. In the first process, toxic alone is removed, whereas in the second, toxic and matrix are removed simultaneously. It is of interest to compare the characteristics and merits of these two types of paint, and also to discuss the fundamental principles in their design which may be deduced from the data in this chapter.

In continuous contact leaching, no steady-state level of the leaching rate is achieved; the leaching rate falls gradually, as extraction proceeds into the paint interior and as the chain of continuous contacts between particles becomes increasingly imperfect. The higher the proportion of toxic, the higher the leaching rate throughout the life of the paint. Thus, increasing the loading will increase the effective life, or the time elapsed before the leaching rate falls below 10 $\mu\text{g./cm.}^2$ /day. On the other hand, increasing the loading will enormously increase the wastage of toxic, because of the high initial leaching rates which result.

The magnitude of such waste may seem overwhelming—since, for example, the initial leaching rate of a paint consisting of 90 per cent of cuprous oxide in Vinylite resin is of the order of 250 $\mu\text{g./cm.}^2$ /day, or twenty-five times the minimum value necessary for antifouling action. Fortunately, the formation of deposits of basic cupric carbonate and oxychloride curbs this waste to some extent; the higher the leaching rate, the greater will be the tendency for deposit formation, with consequent depression of the leaching rate to a lower level. An illustration of the magnitude of the waste which occurs in practice may be obtained from an analysis of the data in Figure 3a. For this purpose, the utilization efficiency may be defined as the ratio of the amount of toxic which would have been lost had a leaching rate of 10 $\mu\text{g./cm.}^2$ /day been maintained throughout the effective life of the paint, to the amount which was actually lost, as estimated from an integration of the leaching rate curves. The utilization efficiency calculated in this way is plotted in Figure 16, together with the paint life, against the weight per cent of cuprous oxide. At 90 per cent loading, the efficiency is about 20 per cent.

The total amount of cuprous oxide lost during the effective life of the paint, divided by the life in months, is also plotted in Figure 16 as "loss per month of life". It represents an average rate of loss which is inversely proportional to the utilization efficiency.

The depth to which the paint has been extracted up to the point when the leaching rate falls below $10 \mu\text{g./cm.}^2/\text{day}$, may be calculated by dividing the total amount of cuprous oxide extracted by the density of the toxic and its volume fraction in the paint. This yields a minimum value, since the extraction is in fact incomplete. Nevertheless, its very small magnitude—far less than 0.1 mm., even for the most heavily loaded paint—emphasizes the thinness of the film which suffices for protection in the case of heavily loaded, continuous contact paints.

Moreover, it is important to note that increasing the thickness of this type of paint does not increase its life. Failure occurs when extraction has proceeded to the critical depth at which imperfections in continuous contact have reduced the leaching rate below the minimal value. The life of the paint should be independent of film thickness so long as the latter exceeds this critical depth.

To summarize, the attributes of continuous contact paints include the advantages of thinness of film and the possibility of achieving an extreme toughness and resistance to abrasion, balanced against the disadvantages of a rather large waste of toxic during the early life of the paint, the lack of a constant level of steady-state leaching, and a rather limited period of effective service. The principles governing the design of this type of paint are as follows: The loading with toxic should be the *maximum* consistent with mechanical integrity, in order to achieve maximum life, even at some sacrifice of utilization efficiency; and the thickness of the film should be the *minimum* in excess of the critical extraction depth, to avoid waste of toxic which would otherwise remain undissolved at the bottom of the film.

In leaching by matrix dissolution, a fairly constant level of the leaching rate is attained in the steady state. This level depends on both the proportion of toxic and the solution rate of the matrix. As long as an adequate steady-state level is maintained, the life of the paint is directly proportional to its thickness. For this reason, it is the life per mil thickness, rather than the total life, which characterizes this type of paint.

The data in Figure 3b, for a series of cold plastic paints, have been analyzed for presentation in Figure 16 along with the continuous contact paints. The life per mil, the utilization efficiency, and the loss per month of life are plotted against the weight per cent of cuprous oxide. The utilization efficiencies of these matrix-soluble paints are very much higher than those of the continuous contact paints, and the toxic losses per month of

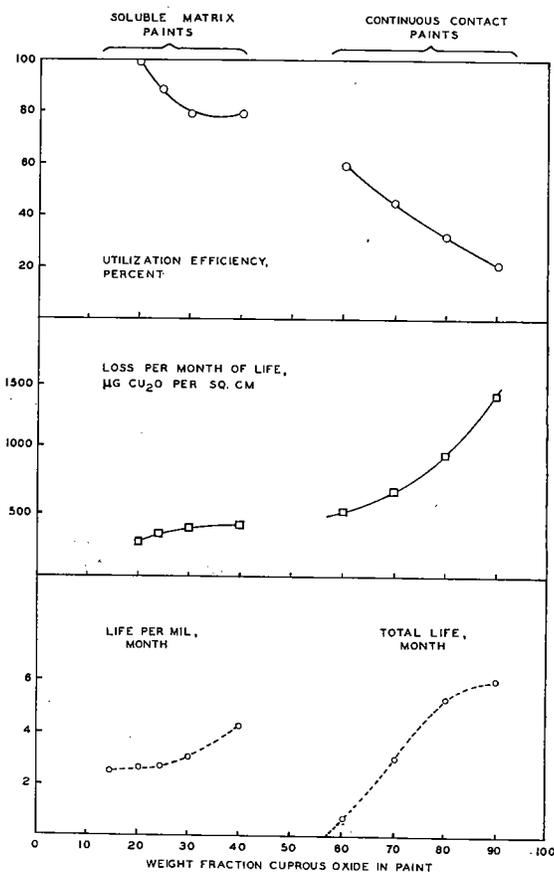


FIGURE 16. Characteristics of continuous contact and matrix dissolution paints: \circ , utilization efficiency; \square , average loss of toxic per month of effective life; \circ , life per mil thickness (matrix dissolution paints), total life (continuous contact paints).

life are correspondingly lower. These data, of course, represent the behavior of a series of paints in a given matrix which has a certain dissolution rate. At a higher matrix dissolution rate, the curves for efficiency and life would be lowered, and that for loss per month would be raised.

The general principles for the leaching behavior of matrix-soluble paints, which have already been discussed on p. 288, are as follows. The lower the toxic loading, the thicker the film required to provide a given life of effective service. Since the wastage of toxic increases with the degree of loading, low loadings should be preferred. However, the lower the loading, the higher the matrix dissolution rate must be to achieve a given leaching rate (equation 4). A fairly large factor of safety must be chosen to allow for possible depression of the leaching rate by deposit formation or accumulation of insoluble matrix ingredients, as well as the possibility of accelerated paint removal by erosion.

The attributes of matrix-dissolving paints include as advantages the possibility of attaining a constant level of steady-state leaching with a

relatively small waste of toxic—not more than that consistent with a reasonable factor of safety—and the possibility of providing a very long life of active service by employing a thick paint film. In addition, the opportunity of making independent adjustments of two variables—the degree of loading and the matrix dissolution rate—permits far greater flexibility in designing a paint with the desired leaching rate. The disadvantages of matrix-dissolving paints are the greater thicknesses required, and the fact that most soluble matrices are comparatively soft and may not stand up under extreme conditions of erosion. The principles governing the design of this type of paint are quite different from those of the continuous contact type. The loading with toxic should be the *minimum* which, for a matrix with a given dissolution rate, would provide an adequate steady-state leaching rate with a suitable factor of safety; and to achieve a maximum life, the thickness of the film should be the *maximum* consistent with economy and mechanical stability.

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