

The Dissolution of the Matrix and Its Ingredients

Although the matrix is at least as important as the toxic, the properties which make certain matrix ingredients useful for the formulation of antifouling paints have often not been recognized. As shown in the previous chapter, some paints depend upon the solubility of a matrix ingredient to maintain an adequate steady-state leaching rate of the toxic. The slowly dissolving matrix eventually exposes toxic particles which lie deep within the paint film, thus permitting them to dissolve and exert their toxic effect on the fouling organisms. Thus the toxic and the matrix dissolve simultaneously, resulting in a gradual decrease in thickness of the film. Since the toxics commonly used dissolve more rapidly than the matrix ingredients, the rate of solution of the latter controls the rate of solution of the entire film. This chapter summarizes the current knowledge concerning the factors affecting the rate at which certain matrix ingredients dissolve in sea water.

For convenience, the factors controlling the solution of matrix materials may be divided into two classes: those arising from the nature of the dissolving medium employed, and those inherent in the matrix film itself. In the first group of factors we must consider the chemical composition of the dissolving solution, such as its alkalinity and the nature of the salts it contains. The second group of factors includes the chemical composition of the matrix film, the proportion and nature of acidic and neutral materials, the number of phases present, and such physical properties as smoothness and hardness. In addition, the time elapsed between the mixing of the paint and its application, the conditions under which the mixture was prepared, and the age of the paint film itself on the panel or ship bottom may influence the solution rate.

Many acidic resins are soluble in sea water. Their dissolution requires the formation of soluble alkaline salts, and they are not, consequently, soluble in neutral or acid aqueous solutions. Such resins are rendered insoluble if the free acid group of the molecule is neutralized by esterification or by the formation of an insoluble salt or soap. Paint technologists have commented on the acidic nature of natural resins and have suggested modifying them to overcome this "difficulty," or have even stated that they cannot be used in

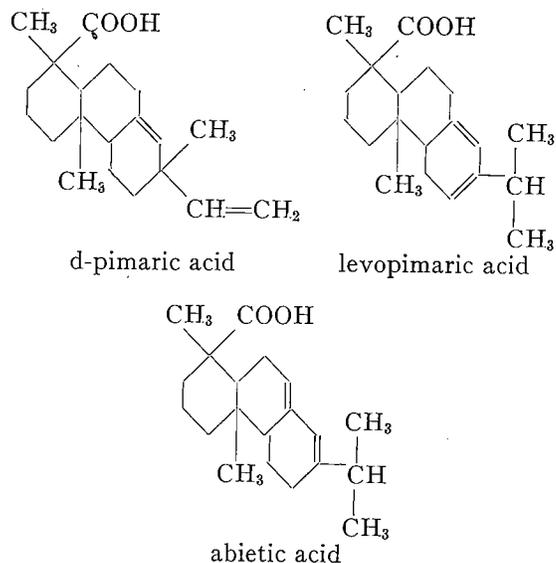
paints because of their tendency to react with pigments (1, 8). Yet this very acidity and the resultant solubility in sea water is the principal reason for the satisfactory performance of antifouling paints containing such ingredients.

THE COMPOSITION OF ROSIN AND ITS DERIVATIVES

The use of rosin as a constituent of antifouling paints was patented in 1867 (3), and since that time, because of its availability and cheapness, its use has been constantly expanded. Its only serious competitor has been shellac, another acidic resin from natural sources. But shellac suffers from the drawback that it must be imported into the United States, a fact that led the Navy in 1926 to discontinue its use (1). The reason for the effectiveness of rosin was not known until 1943, when investigations at the Mare Island Navy Yard and the Woods Hole Oceanographic Institution simultaneously showed that its virtue depended upon its solubility (5, 9).

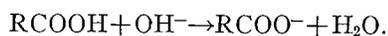
Rosin is obtained from the exudation of pine and fir trees, the greater portion of the world's supply coming from *Pinus palustris* (the longleaf pine) and *Pinus carribea*. The fresh gum, or oleoresin, is subjected to steam distillation to remove the low-boiling volatile fraction known as turpentine. The residual material, crude rosin, is a dark amorphous solid at room temperature. It is composed of about 90 per cent of acidic materials, called resin acids, and about 10 per cent of neutral materials that are apparently non-volatile sesqui- and diterpenes. The resin acids all have the empirical formula $C_{20}H_{30}O_2$, and consist of a mixture of substances the nature of which is not yet entirely clear (6). The acids are known to comprise a mixture of the acid-stable d-pimaric acid and a series of acids (levopimaric acid, the sapinic acids, etc.) which are all converted by boiling with mineral acid into abietic acid, a substance that represents a relatively stable stage in a series of complex changes. The formulas of three of these compounds are given on the next page (6).

Methods have been developed for the determination of both d-pimaric acid (11) and levopimaric acid (7) in resin acid mixtures. In the original oleoresin from which rosin is prepared, it has been found that the acid fraction contains 38 per cent



d-pimaric acid and 36 per cent levopimaric acid, the balance consisting entirely of those intermediary acids that are convertible into abietic acid. There is no evidence that any abietic acid exists as such in oleoresin. In commercial rosin the isomerization process probably takes place to some extent during the process of steam distillation, and abietic acid may be present in amounts depending upon the extent of the heat treatment. Rosin is graded according to its color, and is purified, generally by solvent extraction, for the purpose of removing the color bodies present (10).

The resin acids of rosin contain two carbon-carbon double bonds and one carboxyl group per molecule. The former give rise to the characteristic instability of rosin, while the latter enables rosin to be dissolved in alkali, though the acid itself is quite insoluble in neutral or acid aqueous solutions. The resin acids dissolve in the form of the resin ion, which is formed by the attack of the hydroxyl ion of the alkali:



The resin ion will stay in solution as long as there is no substance present that will react with it to form an insoluble compound. In sea water the resin ion reacts to a certain extent with calcium and magnesium ions to form the corresponding insoluble soaps. This reaction may also take place on solid rosin surfaces, and in this way the rosin becomes at least partially covered with insoluble material, which effectively cuts down the solution rate in sea water.

When the carboxyl group of a resin acid is esterified with a mono- or polyhydroxy alcohol, an alkali-insoluble ester is formed. The esters formed

from rosin and low molecular weight alcohols, such as methyl and ethyl alcohols, are far softer than rosin, while those formed from polyhydroxy alcohols, such as glycol or diethylene glycol, are usually harder and more brittle than rosin.

It should be pointed out that these modified rosins are mixtures, as is the parent substance. In addition, the esterification is never complete, so that the product always contains some acid material. The following compounds are typical rosin esters. The trade name of the material used is given in each case. In these formulas RCOOH is used to represent the resin acid.

Methyl Abietate (Abalyn)

RCOOCH_3 This material is 92-94% neutral and is liquid at room temperature.

Glycol diabietate (Flexalyn)

$\text{RCOOCH}_2-\text{CH}_2\text{OOCR}$ This material is 94.5% neutral and softens at 45-50° C.

Glyceryl triabietate (Ester Gum)

$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \\ \text{C} \quad \text{C} \quad \text{C} \\ \text{R} \quad \text{R} \quad \text{R} \end{array}$ This material is 94% neutral, melts at about 100°C., and is quite brittle.

Pentaerythritol esters of rosin (Pentalyn M)

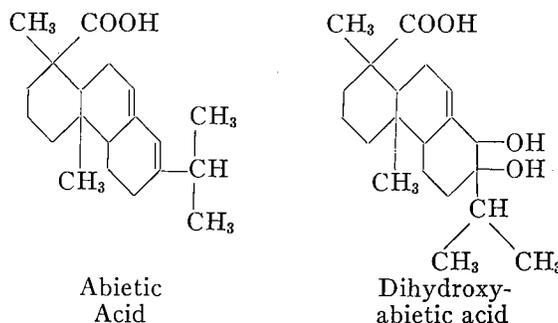
$(\text{HOCH}_2)_3\text{C CH}_2\text{OOCR}$ This material consists of a mixture of all four possible rosin esters of pentaerythritol, the higher molecular weight ester predominating. It melts at 165° C., and is 97.5% neutral.

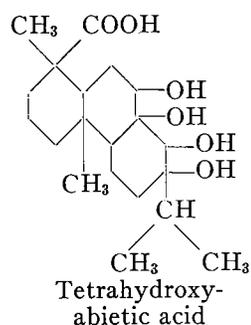
$(\text{HOCH}_2)_2\text{C} (\text{CH}_2\text{OOCR})_2$

$\text{HOCH}_2 \text{C} (\text{CH}_2\text{OOCR})_3$

$\text{C} (\text{CH}_2\text{OOCR})_4$

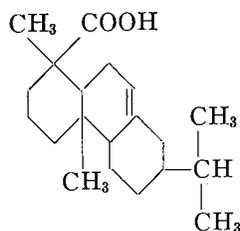
The properties of rosin are also changed when the double bonds of the resin acids are modified. The double bonds of abietic acid oxidize readily, as evidenced by the fact that freshly prepared abietic acid becomes quite yellow after a few days. This reaction is represented as follows:



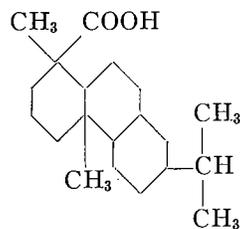


The first step of the oxidation is the more rapid and attacks the more sensitive of the two double bonds. This oxidation increases the acidic properties of the rosin, making it dissolve more rapidly in alkaline solutions.

Hydrogenation of the double bonds reduces the acid strength and decreases the solubility of the product in alkali. Staybelite resin is rosin hydrogenated by the addition of one and one-half moles of hydrogen to each mole of abietic acid, and consists of about equal proportions of dihydro- and tetrahydroabietic acid:



Dihydroabietic Acid



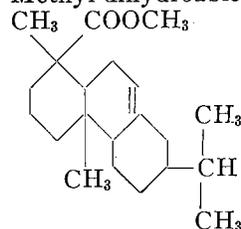
Tetrahydroabietic Acid

The reduced acids are much more resistant to air oxidation than the parent resin acids.

The double bonds can also be partially saturated by the addition of various organic compounds. The maleic anhydride adduct and the dimer of rosin (Poly-Pale resin) are examples. It is probable that many other modifications of this sort could be made. The solubility of such a modified rosin, provided the acid group is not chemically combined, will depend upon whether the substituted group increases or decreases the acid strength of the molecule.

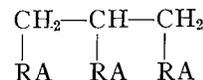
If the rosin molecule is esterified and the double bonds are partially saturated as well, resins which are insoluble in alkaline solutions and resistant to air oxidation are obtained. Some examples of these modifications are given below.

Methyl dihydroabietate (Hercolyn)

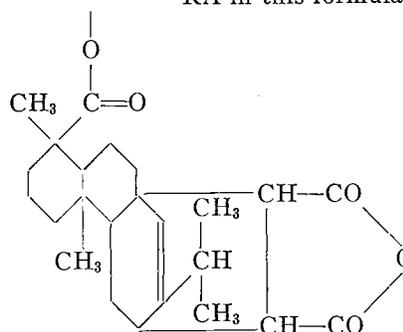


This material is 99% neutral and is liquid at room temperature.

Maleic anhydride adduct of glyceryl triabietate (Lewisol 33)

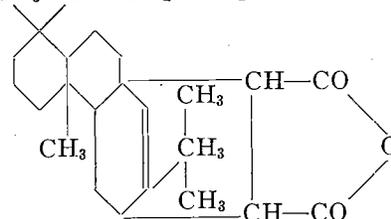
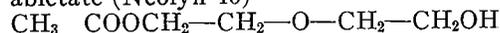


RA in this formula is:



This material is 97.5% neutral; it softens over the range 152-168° C.

Maleic anhydride adduct of diethylene glycol monoabietate (Neolyn 40)



This material is a viscous liquid with an acid number of 20-25.

DISSOLUTION OF ROSIN IN SEA WATER

Various methods have been used to study the dissolution of rosin and other acidic resins in sea water. Darsie (4) measured the rate of solution of rosin from a fiber in sterile sea water by the decrease of its diameter. The initial rate of solution calculated from his data was 250 $\mu\text{g./cm.}^2/\text{day}$. It gradually decreased with continued soaking until after about three days it became uniform at 54 $\mu\text{g./cm.}^2/\text{day}$. Studies of the weight loss (10) of small panels coated with rosin and various paint matrices in sterile sea water gave initial rates of solution of from 100 to 500 $\mu\text{g./cm.}^2/\text{day}$, and steady-state rates after some time of 12 to 100 $\mu\text{g./cm.}^2/\text{day}$.

Calculation of rates of solution in this way from measurements of change in weight or thickness may conceivably be falsified through the loss of material from the rosin surface through other mechanisms than dissolution—abrasion, for example—and through gains in weight due to deposits from the solvent or imbibition. To eliminate this uncertainty, the dissolved rosin can be determined directly by recovering it from the filtered sea water solution by acidification of the solution and extraction with an organic solvent. Using a large volume of flowing solvent and a continuous extraction procedure, substantial amounts of rosin can be recovered. The amounts of rosin, dissolved in a 24-hour period from panels agitated in running sea water, recovered in this way are shown in Table 1. They range from 123 to 1,460

TABLE 1. Dissolution of Rosin in Running Sea Water from a Panel 155 cm.² in Area Stirred at 85 R.P.M. for 24 Hours. The Effluent Sea Water was Continuously Extracted with Chloroform

Drying Time of Panel days	Volume of Sea Water Used liters	Total Rosin Dissolved mg.	Rosin Dissolved $\mu\text{g./cm.}^2$
1	24.5	19	123
2	29.5	21	135
6	12.0	37	239
7	13.0	49	316
14	14.0	62	400
93	20.0	173	1117
99	17.0	177	1140
102	20.7	226	1460

$\mu\text{g. per cm.}^2$ dissolved in a 24-hour period, and thus agree in order of magnitude with the solution rates measured by change in weight or thickness. Following the discussion of steady-state leaching rates in Chapter 16, it is apparent from these data that the rate of dissolution of rosin in sea water would be ample to provide for continuous liberation of the toxic from an antifouling paint with a rosin matrix.

The rosin samples used in this experiment were aged after application to the panels for various periods of time before the test, and the amount dissolved increases with the increasing age of the panel. This effect will be discussed at greater length below.

The decrease in the rate of solution of rosin from a panel after the first day or so in sea water is also shown by direct recovery. Table 2 presents results obtained during 3 successive 24-hour periods of extraction of a panel dried for 14 days, and two extractions from a panel dried for 93 days.

The method of direct recovery by continuous extraction is so time-consuming that most studies of dissolution rates have been carried out in arti-

TABLE 2. Amount of Rosin Dissolved During Successive 24 Hour Periods of Extraction in Running Sea Water from Rosin Coated Panels 155 cm.² in Area Rotated at 85 R.P.M. The Effluent Sea Water was Continuously Extracted with Chloroform

Drying Time of Panel days	Extraction	Volume of Sea Water liters	Total Rosin Dissolved mg.	Rosin Dissolved $\mu\text{g./cm.}^2$
14	first	14.0	62	400
14	second	19.7	31	200
14	third	20.0	36	232
93	first	20.0	173	1117
93	second	9.5	68	439

ficial solutions in which both the solubilities and the rates of solution of acidic resins are higher than in sea water. The use of artificial solvents also permits variation of composition to determine the effects of such variables as pH and salt concentration, and avoids some of the complications of the mixture of ions occurring in sea water.

Effect of the Composition of the Aqueous Solvent on the Dissolution of Matrix Ingredients

The important properties of the aqueous solvent are its temperature and such chemical properties as the pH and the amount and kind of dissolved salts. In sea water the pH varies within the limits of about 7.5 to 8.2, the higher values being more common. The buffering action of sea water is the result of the presence of carbonate and bicarbonate ions, together with a small amount of borate. The sodium chloride content of sea water is 0.48 mole per liter; magnesium is present in about 0.05, and calcium in about 0.01 mole per liter. As will be seen, all of these constituents have been found to influence the solution rate of rosin.

Effect of pH of the solvent: The solubilities of

TABLE 3. The Solubilities of WW Rosin and Abietic Acid* in Aqueous Alkaline Solutions

Final pH	Equilibration Time hours	Solubility $\mu\text{g./cc.}$	Log Solubility
Rosin			
6.9	18	29	1.46
7.1	41	52	1.72
7.25	72	52	1.72
7.3	45	67	1.83
7.4	19	62	1.79
7.5	65	66	1.82
7.6	45	88	1.94
8.1	18	439	2.64
8.80	2.3	1494	3.17
Abietic Acid			
7.80	48	56	1.75
8.10	72	514	2.71
8.33	24	382	2.58
8.60	72	2040	3.31
8.68	—	2212	3.34
9.17	24	3578	3.55

* The abietic acid was prepared from rosin by acid isomerization by Steele's method (12). Material with a rotation of -45° in alcohol was used. The optical rotation of pure abietic acid is -102° in alcohol.

WW rosin and abietic acid have been estimated by equilibrating an excess of the powdered material with distilled water made alkaline with sodium hydroxide, and recovering the dissolved resin from the filtered aliquot of the solution by acidification and extraction with ether (11, 13). The results obtained are given in Table 3, and the logarithm of the solubility is plotted in Figure 1

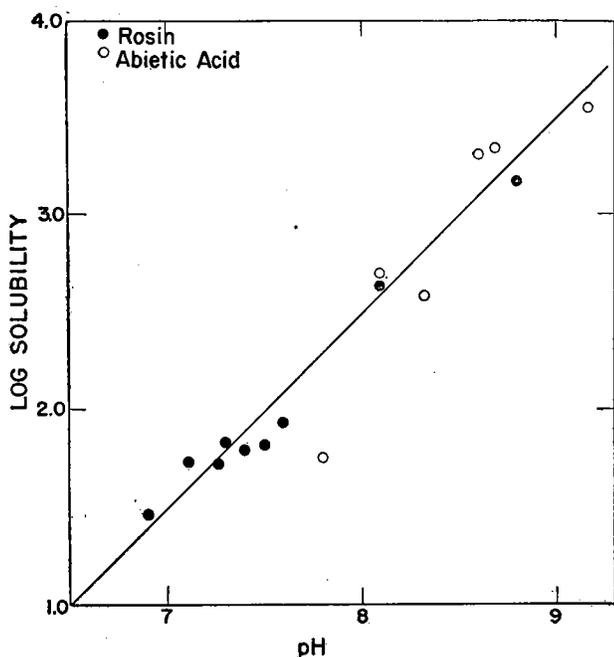


FIGURE 1. The logarithm of the solubility of WW rosin and abietic acid as a function of the pH of the aqueous solvent.

against the pH of the solvent at the end of the equilibration. The data for abietic acid and WW rosin are in close agreement and fall approximately on a straight line with a slope of 1, showing that the solubility is proportional to the hydroxyl ion concentration. This relation is strong evidence for the belief that the dissolution of rosin and abietic acid involves formation of an alkaline salt.

Studies of the rate of solution of WW rosin from plane surfaces have shown that this too, like the solubility, increases with increasing pH of the solvent. The results of an experiment designed to determine the effect of pH on solution rate are shown in Figure 2, where the amount dissolved is plotted against time.

These relationships show that it is possible to accelerate the dissolution of acidic resins by using more strongly alkaline solutions. This principle is the basis of the acid-alkali and glycine accelerated tests for antifouling paints which were discussed in Chapter 16. Certain limitations of using strongly alkaline solutions should be pointed out,

however. These solutions may hydrolyze some neutral resinous salts. Copper resinate, for example, has a negligible solubility in sea water, but is readily dissolved by an alkaline glycine buffer solution of pH 10.5, with accompanying hydrolysis. The solubilities of such compounds in strongly alkaline solutions do not, therefore, necessarily enable one to predict their solubilities in sea water. A further complication arises since the salts normally present in sea water modify the solubility of the resins. This effect will be discussed below.

Effect of sodium chloride content of the solvent: The influence of sodium chloride on the solubility of WW rosin has been investigated by employing as solvents sodium chloride solutions of various concentrations. A maximum solubility was found at a sodium chloride concentration of about 0.034 M.

The influence of sodium chloride on the rate of solution of a resin mixture has been studied by measuring the amounts of resin dissolved from Navy standard cold plastic paint matrix¹ by buffer solutions at pH 9.0 containing various amounts of sodium chloride. Table 4 gives these results and shows that the rate of solution, also, goes through a maximum with increasing concentration of neutral salt. In this case the maximum occurs at 0.24 M.

Effect of calcium and magnesium content of the solvent: The divalent salts of rosin and similar acid resins are generally insoluble in alkaline solutions. The presence of calcium and magnesium in

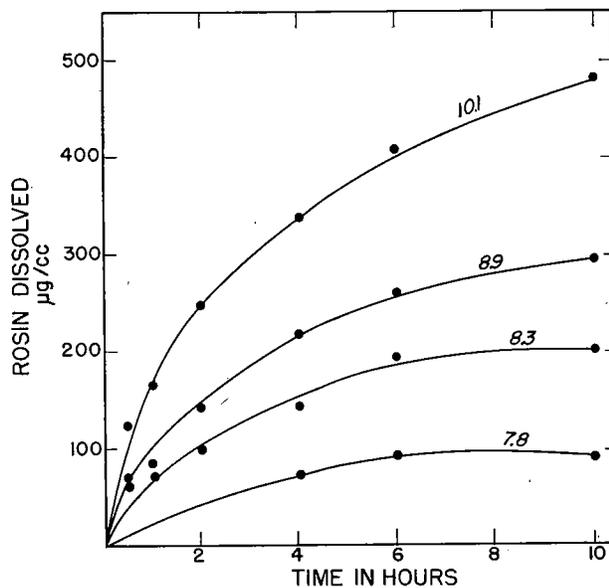


FIGURE 2. The dissolution of rosin from panels by alkaline buffers. The initial pH of the buffer used is given at the end of each curve.

¹ This contains a phenol-formaldehyde modified rosin and a small percentage of chlorinated rubber dissolved in coal tar naphtha.

the sea water permits the formation of insoluble salts on the surface of a solid phase of resin, with a resulting decrease in dissolution. Furthermore, the amount of rosin dissolved from a plane surface of rosin by a borate buffer is diminished by addition of small quantities of calcium and magnesium to the solvent. An experiment which illustrates this effect is given in Table 5.

Barnes (2) has determined the calcium content of varnish films after 80 days' exposure in the sea. The high-rosin varnishes contained larger amounts of calcium than did low-rosin varnishes. In a

TABLE 4. Effect of Sodium Chloride Concentration on the Rate of Solution of 143 Matrix from Panels 155 cm.² in Area Immersed in One Liter of Borate Buffer Solution of pH 9.0

NaCl in Buffer moles/liter	Concentration of Ether Soluble Material (mg./l.) after		
	4 hours	26 hours	50 hours
0	94	138	144
0.24	444	765	784
0.48	386	635	617
0.96	196	410	398

rosin-ester gum series, the amount of calcium was directly correlated with the concentration of rosin.

The retarding action of the calcium and magnesium ions is apparently due to the formation of the insoluble salts of calcium and magnesium abietate on the surface of the rosin. These salts may be recovered from the surface by soaking in dilute hydrochloric acid. Apparently they slowly cover the rosin surface and hinder the dissolving action of the alkali.

The data in Table 5 show that sea water dissolves less rosin than does a borate buffer containing an equivalent amount of calcium and magnesium. The boric acid content of the buffer solution used, 0.05 M, is about one hundred times that normally present in sea water. The addition of boric acid to sea water, up to the amount used in these buffers, results in an increase in the amount of rosin dissolved, showing that boric acid itself has a solvent action on the rosin. The results of an experiment, which illustrates this effect, are given in Table 6. The addition of only 0.01 M boric acid increases the amount of rosin dissolved to nearly the same value obtained for the buffer solution containing 0.05 M borate, sodium chloride, and the appropriate amounts of calcium and magnesium (Table 5). Further additions of borate result in no increase in the amount of rosin dissolved, owing presumably to the progressive decrease in the pH of the solution.

To summarize the important characteristics of the solvent, it is apparent that pH, the salt

TABLE 5. The Dissolution of WW Rosin in Borate Buffer Solutions to which Calcium and Magnesium Were Added, and in Sea Water

	Concentration of Added Ions		Final pH	Total Dissolved Rosin After 24 hours
	Ca moles/l. ×10 ³	Mg moles/l. ×10 ³		
Borate Solutions	0	0	7.73	393
	1.25	0	7.72	380
	2.25	0	7.73	364
	5.0	0	7.73	334
	10.2	0	7.72	317
	0	0	7.82	417
	1.25	0.7	7.82	370
	2.5	1.3	7.81	331
	5.0	2.7	7.78	316
	10.2	5.3	7.71	278
	Content of Ca and Mg Ions		Final pH	Total Dissolved Rosin After 24 hours
	Ca moles/l. ×10 ³	Mg moles/l. ×10 ³		
Sea Water	10.2	5.3	7.64	184
	10.2	5.3	7.63	176

content, and the presence of ions, which may either form insoluble resinates or exert a solvent action on the resin, will influence the results obtained in studies of the solubility and rate of solution of matrix materials. It should be pointed out that the pH of the solvent has an opposite effect on the dissolution of the matrix to that described in Chapter 15 on the solution of the toxic. In paints which maintain their adequate leaching rate by virtue of a soluble matrix, variations in the pH of the sea water may therefore be expected to have a complicated effect. In estuarine waters, where the pH is frequently lower than in normal sea water, the rate of solution of the matrix will decrease. In spite of the increase in the solution rate of the toxic, the net leaching rate of the paint may be expected to be lower, since, according to Equation (4) of Chapter 16, it is the intrinsic solution rate of the *matrix* which primarily determines the toxic leaching rate of this type of paint.

It is clear that the principles controlling the dissolution of acid resins can be studied in alkaline buffer solutions which accelerate their rate of dissolution. This conclusion is the foundation of the two accelerated paint tests described in

TABLE 6. Effect of Additions of Boric Acid to Sea Water on the Amount of Rosin Dissolved from Panels Coated with WW Rosin. (Panels 8 Months Old, Stirred 8 Hours)

H ₃ BO ₃ Added moles/l. ×10 ³	Final pH	Dissolved Rosin
0	7.64	169
10	7.45	243
19	7.33	250
29	7.20	236
39	7.14	219
50	7.08	231

TABLE 7. Amount of Resin Dissolved from 3"×4" Panels Rotated in a Glycinate Buffer Solution (pH=10.6) for Six Hours

Resin Tested	Acid Number	Dissolved Material μg./cm. ²
Neolyn 20	10-15	70
Lewisol 33	40	80
Estergum	10	110
Neolyn 40	20-25	120
Pentalyn M	25	130
Hercolyn	8	250
Rosin	165	>8000

Chapter 16. The experiments described in the remainder of this chapter have been conducted mainly in alkaline buffer solutions.

Effect of the Composition and History of the Matrix Film on its Dissolution

Since the resins dissolve by the formation of soluble salts, only those resins whose molecules have free acid groups can be dissolved by the slightly alkaline sea water. In molecules having two or more acid groups, the acid number² can be modified by partial neutralization or esterification. Abietic acid, the main constituent of rosin, however, has only one free acid group. Any decrease in its acid number by partial neutralization consequently represents a mixture of neutral and unchanged material. The strength of the acid also influences the rate of solution of the resinous material, stronger acids dissolving more rapidly. Any modification of the abietic acid molecule which increases the dissociation constant of the acid group results in increased rate of dissolution, and vice versa.

Effect of the acid number of rosin and its modifications: Since the neutralization of the acid group of rosin completely neutralizes the molecule, the products of such reactions are virtually insoluble in sea water. The reactions, however, are rarely complete, and some unmodified rosin acid is

TABLE 8. Amount of Material Dissolved from Mixtures of Rosin with Neolyn 20 and Hercolyn in Glycinate Buffer (pH 10.5). One Panel (155 cm.²) Rotated at 80 R.P.M. for Six Hours in 1.35 Liters of Buffer

Ester Used	Composition		Acid Number of Mixture	Total Dissolved μg./cm. ²
	Rosin %	Ester %		
Neolyn 20	90	10	149	7740
	80	20	134	2390
	70	30	119	580
	60	40	103	580
	50	50	88	460
	0	100	10	120
Hercolyn	90	10	149	7180
	80	20	134	5680
	70	30	118	4900
	60	40	102	3340
	50	50	87	2640
	0	100	8	250

² The acid number is defined as the amount of potassium hydroxide in milligrams required to neutralize the free acids in 1 gram of the substance.

frequently present. The amounts of material which may be dissolved from films of some of the rosin derivatives described in the introduction of this chapter are given in Table 7. A strongly alkaline buffer is necessary in order to obtain measurable amounts of dissolved materials from these substances, which are all partially neutralized. The amounts dissolved are very small compared with the value for rosin, which is a minimum figure, since all of the rosin was dissolved from part of the panel in this strongly alkaline solution.

Simple admixture of neutral resinous materials to rosin lowers the acid number. The resulting mixtures also have lower solution rates than rosin. As examples of this effect, the amount dissolved from panels coated with mixtures of two of the above neutral resins with rosin are given in Table 8.

The decrease in the rate of solution caused by these two compounds is not the same; the Neolyn 20 mixtures dissolve more slowly than the Hercolyn

TABLE 9. Rates of Solution of Staybelite, WW Rosin and Oxidized WW Rosin. Borate Buffer pH 9.0

Material	Amount Dissolved in 1 Hour μg./cm. ²
Staybelite	290
WW Rosin	630
"Oxidized" Rosin	3840

mixtures of the same percentage composition and acid numbers. The factors which control the rate of solution of rosin from such mixtures include the hardness of the neutral resin and the physical character of the mixture—e.g., the number of solid phases present. These problems will be discussed at greater length below.

Effect of the modification of the double bonds of rosin: As pointed out in the beginning of this chapter the double bonds of the rosin molecule are oxidized in air, and may be modified, experimentally, by hydrogenation or the substitution of various compounds. The oxidation of these double bonds, which proceeds slowly in air, results in an increase in the solubility of the material. The hydrogenation of the double bonds as represented by Staybelite, a mixture of dihydro- and tetrahydroabietic acid, results in a decrease in the solubility. The amounts dissolved from a panel coated with Staybelite, a freshly prepared rosin panel, and a rosin panel allowed to oxidize in air for 75 days before the test, are given in Table 9.

It is presumed that these changes in solubility which result from the modification of the double bonds, reflect a change in the acid strength of the

molecule. Unfortunately, since rosin and its derivatives are mixtures, no exact determinations of dissociation constants are possible. The change in acid strength as a result of modification of double bonds is, however, sufficiently well established for various other organic compounds to suggest that this is the cause of the observed changes in the solution rates of rosin so modified.

The solution of rosin from panels changes rapidly if they are allowed to dry in air for any length of time. This change in solution rate after various drying times is illustrated in Figure 3, where the amount of rosin dissolved in one hour in borate buffer is plotted against the age of the panel. The rate of solution increased more than tenfold during the 75 days of air drying. Most of this increase occurred during the first 20 days. The amount dissolved from panels aged for various times is plotted in Figure 4 against the time in the solvent. In each case the rate of solution is rapid at first, but decreases during the first hour of extraction. The data plotted in Figure 3 are, therefore, not the maximum rate of solution for rosin of the indicated age.

The increase in solution rate occurs even though

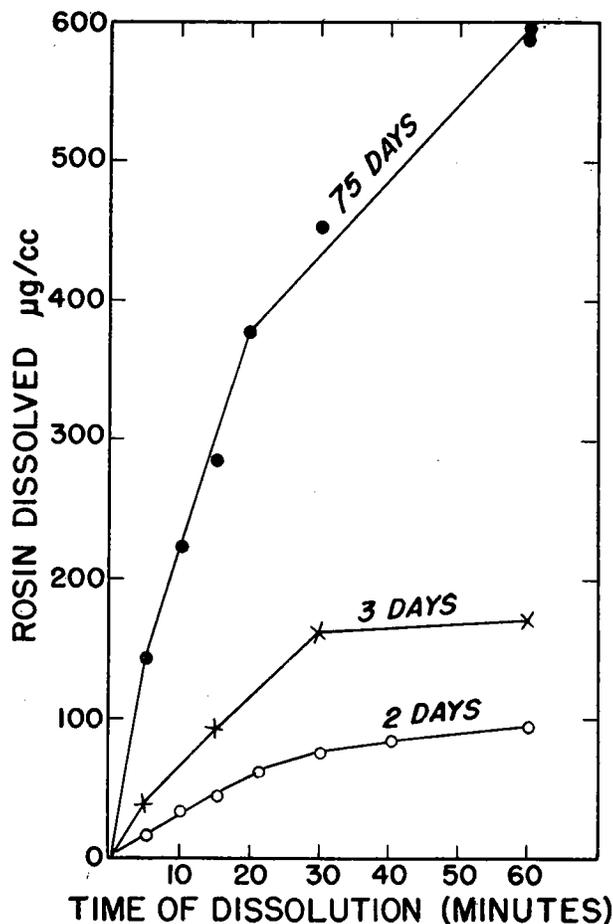


FIGURE 4. The dissolution of rosin from panels in borate buffer (pH 9.0) after various periods of drying in air.

the rosin film is stored under nitrogen to exclude air oxidation. The data in Table 10 show that the amount of rosin dissolved from the panel increases to nearly the same extent after 20 days in nitrogen and in air. The nitrogen used was not specially treated to remove traces of oxygen, which may have been present. Pure colorless abietic acid, even though sealed in a vacuum, will begin to turn yellow after several days. It seems probable that atmospheric oxygen dissolved in the dried layer of rosin is the oxidizing agent.

The oxidation of a film of rosin on a panel extends beyond the surface layer, and may penetrate deeply into the film. The amounts of rosin dissolved from panels aged for various times in air may be used to show the amount of the affected

TABLE 10. Effect of Aging in Nitrogen on the Amount of Rosin Dissolved from a Panel by Borate Buffer in One Hour

Panel Age (days)	Dissolved Rosin (mg.)
0	57
20 (air-dried)	450
20 (N ₂ -dried)	380

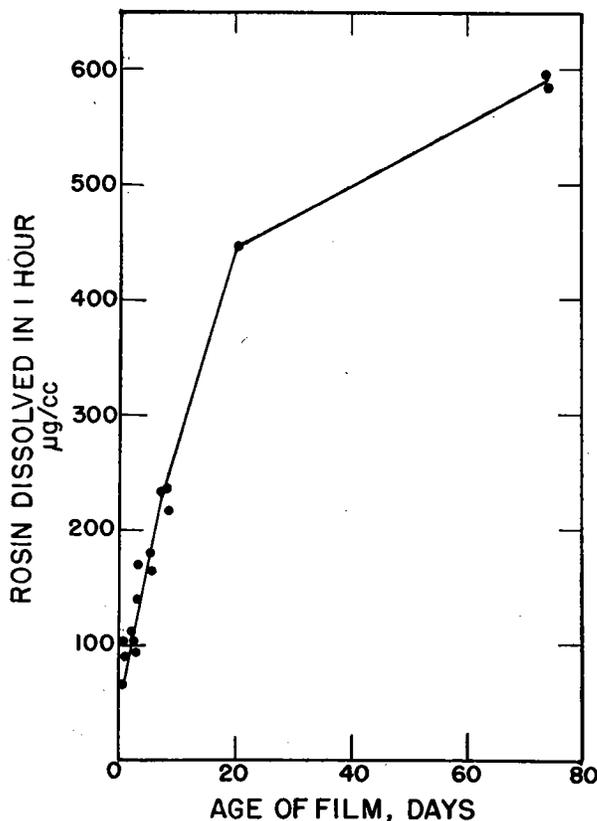


FIGURE 3. Amount of rosin dissolved by borate buffer (pH 9.0) from panels dried in air for various periods of time.

TABLE 11. Formation of Copper Resinate During Storage for 1 Month in Mixtures of Cuprous Oxide and Rosin Dissolved in Equal Parts of Coal Tar Naphtha and Petroleum Spirits

Composition of Mixture		Copper Resinate	
% Rosin	% Cu ₂ O	% of Mixture	% of Rosin Combined
84	16	1.7	1.8
68	32	8.8	12.8
50	50	7.5	13.5
33	67	17.3	47.1

material. The data given in Figure 4 show that both the initial rate of solution from the panel and the total amount of material dissolving during the first hour in the solvent, increase rapidly with the age of the rosin film. This result can mean either that the oxidation process proceeds from the outer surface inwards and that the increase in solubility is a measure of the advancing front of oxidized rosin, or that the oxidation is proceeding uniformly throughout the film and that the increased solubility reflects the increasing proportion of the more soluble oxidation product.

Effect of storage of paint before use: Various reactions and changes may take place in a paint between the time of its manufacture and its use. In antifouling paints containing acid resins and a heavy metal salt as the toxic pigment, the formation of metallic resinates will occur. This reaction results in the removal of soluble matrix and pigment ingredients and in the formation of the insoluble resinate. The data in Table 11 show that almost 50 per cent of the total rosin originally present may be combined in this way during one month's storage when large amounts of cuprous oxide are present. Barnes (2) also found that the amount of copper reacting with the vehicle depends upon the copper content of the paint and is roughly proportional to the milling time up to 24 hours. The type of solvents used and the other ingredients of the paint may also determine how much copper will combine with the acid resins. So many combinations of ingredients are possible that it is manifestly impractical to try to predict how much of an effect this reaction will have in any given formulation.

TABLE 12. Dissolution of Various Grades of Rosin in a Borate Buffer Solution (pH 8.8). The Panels were Dried for 7 Days and Rotated in the Solution for 6 Hours

Grade of Rosin	Rosin Dissolved $\mu\text{g./cm.}^2$
WW	2060
WG	2080
M	1920
H	1900
E	2380
B	1970
FF	920

Oxidation of the rosin in a paint may also be expected to take place to some extent during storage. As discussed above, this could result in an increase in the solution rate of the soluble rosin, though it has been impossible to assess this effect quantitatively.

Solution rates of different grades of rosin: As mentioned previously, rosin is graded by color, which in turn depends upon the amounts of various impurities present. These various grades of rosin, however, have nearly the same acid number and consequently their rates of solution in sea water or alkaline buffers are similar. The data given in Table 12 show that FF rosin is the only one among those studied with a solution rate substantially lower than WW rosin. It appears, therefore, that the specification of the clear rosin grades is unnecessary for use in antifouling paints.

DISSOLUTION OF RESIN MIXTURES IN ALKALINE BUFFERS

The previous discussion has largely been concerned with rosin alone. In actual practice, of

TABLE 13. Ether Soluble Material Dissolved by Sodium Glycinate (0.025M) Solution in Six Hours from Panels Coated with Mixtures of Rosin and Various Neutral Materials

Neutral Material	Age days	Total Amount Dissolved ($\mu\text{g./cm.}^2$) % Neutral Material				
		10%	20%	30%	40%	50%
Vinylite	7	3900	2540	735	280	
Copper Resinate	1-3	2700	3720	4580	3270	3450
Cumarone Indene	1	2030	885	280		
Pentalyn G	1-2	2550	280	65	39	6
Poly-Pale Ester	2-3	2660	2720	1150	0	0
Calcium Resinate	7	3990	3530	3120	3420*	2250*
Mg Resinate	7	4150	2140	2440		
Mg & Ca Resinate	7	3670	1920*	2300*	2220*	2160*
Neolyn 20	7	7730	2380	580	580	465
Hercolyn	7	7120	5690	4900	3340	2640

* Two phases visible on panel.

course, rosin is rarely used as the sole binder of antifouling paints because of its poor physical properties; it is always mixed with other resinous materials.

The resinous materials which are mixed with rosin are generally neutral and insoluble. It is pertinent to inquire, therefore, what effect these admixtures have upon the solution rate of the rosin. All of the neutral materials decrease the rate of solution from a panel, but the effect is quantitatively different for the various substances.

Quantity of neutral resin added: The effect of adding various amounts of different neutral materials on the solution rate of rosin is shown by the data in Table 13. The rate of solution decreases in every case as the proportion of neutral material

TABLE 14. Dissolution of Rosin Vinylite Mixtures of Various Thicknesses in Glycinate Buffer (pH 10.6). The Panels were Dried for One Week before the Test, and Rotated at 85 R.P.M. in 1.35 Liters of Solution

Composition	No. of Coats	Ave. Film Weight mg./cm. ²	Total Dissolved (μg./cm. ²)						Film Dissolved %
			10 min.	30 min.	1 hr.	2 hrs.	4 hrs.	6 hrs.	
10% Vinylite	1	10.0	1040	1710	2300	2880	3480	3900	39
90% Rosin	2	17.7	1060	1430	1910	2560	3210	3660	21
	4	32.0	900	1120	1630	2960	3380	4110	13
21.5% Vinylite	1	5.2	930	1320	1630	1940	2210	2520	48
78.5% Rosin	2	11.1	1120	1710	2080	2500	3030	3360	30
	4	18.2	1090	1650	1890	2210	2590	3060	17
30.5% Vinylite	2	11.3				496	470	735	6
69.5% Rosin	4	25.6				490	555	860	3
	6	38.8				450	612	825	2
40.5% Vinylite	2	12.1						310	2.5
59.5% Rosin	4	23.6						290	1.2
	6	40.0						284	0.7

is increased. The magnitude of the effect at any given concentration of neutral material, however, varies widely. The solution rates of those mixtures in two phases which were visible on the panel remain high despite considerable additions of neutral material. The liquid Herculyn also permits high solution rates even when it is present in considerable amounts. It is possible that this is the result of an ability of Herculyn to flow off the panel as it is uncovered by the dissolving rosin.

Barnes (2) shows that the amount of rosin dissolved in the sea is directly related to the amount of rosin in the mixture. Below about 30 per cent rosin, little or no loss of rosin occurred. Analyses of the residue on the panel indicated that measurable amounts of rosin acids remained in the binder skeleton. In a rosin-Bedesol mixture which originally contained 75 per cent rosin, the concentration of rosin left after 40 days soaking in the sea was somewhat greater than 20 per cent to a depth of 30μ. Between 30 and 80μ the concentration gradually increased, and was the same as the original composition at greater depths. Barnes concluded that a portion of the acid resin is readily dissolved, and that the binder skeleton which remains contains about 20 per cent acid resin, which is dissolved much more slowly.

Effect of thickness of film: If a mechanism exists to permit the solution of the soluble material throughout the depth of the film, a partial extraction should dissolve the same amount of soluble material, regardless of the film thickness, provided of course that the film is at least as thick as the depth of extraction. The results of extraction of mixtures containing approximately 10, 20, 30, and 40 per cent Vinylite in rosin and applied in different thickness are given in Table 14. As the

Vinylite content of the mixtures was increased, the amount of dissolved ether soluble material decreased. For each composition, essentially the same amount of ether soluble material—i.e., rosin acid—was dissolved, regardless of whether one or more coats of the mixture were applied. As a result the percentage of the original film which dissolved decreased as the thickness of the film was increased. The rate of solution fell off as the extraction proceeded into the mixture, but the thickness of the film did not influence the course of extraction over the period of this experiment. For each neutral material studied, a maximum permissible concentration will be found. If the neutral material is added in concentrations greater than this critical value, only very little rosin can be dissolved, and the rate of solution from the

TABLE 15. Amount of Rosin Dissolved in Glycinate Buffer in Six Hours from Mixtures Containing 20% Neutral Materials (pH=10.6)

Neutral Material	Acid No. of Neutral Material	Softening Point of Neutral Material °C.	Total Dissolved μg./cm. ²
Ester Gum			940
Pentalyn X	15	155	1460
Pentalyn G	19	131	1770
Pentalyn M	25	165	1860
15% MgR ₂ } 5% CaR ₂ }	0	—	1920
Neville G	0	—	2120
MgR ₂	0	—	2140
Neolyn 20	10-15	72-78	2380
Hydroabietyl Alcohol	0	33	2710
Pentalyn A	19	110	3000
CaR ₂	0	—	3530
Vinylite	0	—	4320
CuR ₂	0	—	4380
Poly-Pale Ester #1	8-10	80-85	4350
Flexalyn	5-10	45-50	4750
Poly-Pale Ester #3	8	—	4760
Lewisol 33	40	152-168	4900
Herculyn	8	Liquid	5500
Hydrogenated Ethyl Abietate	8	Liquid	5900
Neville R-29	0	Liquid	6550
Neolyn 40	—	—	6750

mixture will never be sufficient to permit steady-state leaching of the toxic from a paint in which it is used as a matrix.

Effect of the nature of the neutral material: The effect of adding various neutral materials to rosin at a concentration of 20 per cent has been studied with several substances. The results obtained are listed in Table 15 in order of the increasing amount of rosin which can be dissolved from the mixture. It will be noticed that the four resins permitting the greatest solution are liquid. In general, the remaining materials are arranged approximately in order of their softening points. It thus appears that the harder neutral materials have a more pronounced depressing effect on the solubility of rosin than do the softer ones. In other words, plasticizers may be added to paint films in relatively high concentrations without exerting too detrimental an effect on the solubility of the matrix. Tougheners, on the other hand, must be added judiciously in small quantities in order to avoid making the matrix insoluble.

Significance of Matrix Solubility

To be effective an antifouling paint must contain a toxic which is slightly soluble in sea water, compounded in a matrix in such a way that it can be released at an adequate, uniform rate. If the matrix is insoluble, enough toxic must be incorporated to give continuous contact between the toxic particles. If, however, the matrix is soluble in sea water, less of the toxic is required, and the solution of the matrix controls the toxic leaching rate. These mechanisms of release of toxic are discussed in detail in Chapter 16.

The present state of knowledge of matrix ingredients permits qualitative predictions of the solubility in sea water of many matrix mixtures. In general, therefore, the type of paint in which they would be satisfactory can be decided in advance. However, the solution rates to be

expected, and consequently the toxic loading required to give satisfactory results, vary so greatly, depending upon the nature of the neutral material included, that quantitative predictions are as yet untrustworthy. Each combination of matrix ingredients must be studied individually in order to design the paint most effectively. Chapter 19 discusses the design of antifouling paints in detail.

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