Fouling Organisms.

(macro-organisms in sea water and their effect on corrosion)

Many thousands of species of invertebrate animals and marine plants have been described and named.
In some locations, even far from shore, pelagic marine life is so prolific and forms such dense mats on the surface of the sea that the speed of a ship may be appreciably reduced.
Only a few kinds of these animals and plants should be considered as fouling organisms.
The vast majority are free swimming and do not possess the necessary organs or have the power to become attached to any material.
Others must burrow in mud, sand, or other substance in the sea for protection in order to survive.
None of the vertebrates, such as the fish or mammals which are so plentiful in salt water, are capable of maintaining a permanent foothold on any material and none, therefore, should be considered as being true fouling organisms.
Organisms which might affect metals or other submerged materials in salt water can be roughly divided in to three groups:
- sessile organisms
- semi-motile fouling organisms
- motile organisms

Sessile Organisms.

This group cannot survive without becoming firmly attached to a suitable base.
All organisms found firmly attached to a material in salt water secured this attachment while still in a very minute embryonic form.
No organisms have the ability to become firmly attached to any base after having passed from the minute embryonic form to the nature form.
No true fouling organism can change its position once it has become attached.
Very few can survive if they become separated from the base upon which they have grown, and none which has become attached has the power to secure a new foothold.
The following list includes most of the common forms of true sessile fouling organisms:

A) Organisms which built calcareous or chitinous shells;
1. Annelids, which form coiled or twisted tubes.
2. Barnacles, which built cone-shaped shells built up of laminated plates.
3. Encrusting Bryozo, colonial animals which form flat, spreading, multi-cellular,
4. coral-like patches.
5. Mollusks, including several species, such as oysters and mussels.
6. Corals.

B) Organisms without hard shells;
1. Marine algae: green, brown, or red filament-like growths which occur usually near the water line and include such forms as "Ceranium"
"Fucus"
"Polysiphonia"
"Ulva"
2. "Filamentous Bryozoa"-fern-like or thre-like growths.
3. Coulenterates (hydroids) such as "Tubularia" with stalk-like or branching Growths, each branch terminating in an expanded tip; also "Bougainvillia" And "Campanularia"
4. Tunicates (sea squirts); soft, spongy masses.
5. Calcareous and siliceous sponges.

All the above are completely sessile fouling organisms. There are, however, other animals which may occasionally contribute to some extent, since they are semi or optionally motile.

Semi-Motile Fouling Organisms.

Some of the organisms may become attached early in life and remain on the same spot until the die.
Other organisms may grow on all sidus, thus preventing any change of position.
Unless completely covered and thus deprived of food and water, they can survive and thrive, but they have the power of locomotion and frequently do move from one location to another.
They include:

1. Sea anemones and allied forms, flower-like animals which may become firmly fastened to metals or other materials, but they also have the ability to move very slowly by sliding along over a mucilaginous slime which they excrete.
   However, even when in motion, these animals are in firm contact with the base upon which they are living.
2. Some of the worms which construct more or less temporary, looseley adherent Tubes of mud and sand for protection. These organisms can readily and frequently do, abandon these tubes, which may be 8-or more inch in length (or 20 cm >) and Move to another location. The old tubes are left behind and contribute to fouling.
3. Certain Crustacea, such as "Corophium", build small temporary sand and mud Tubes which they cement to materials submerged in salt water.
   The tubes are quite adherent, but the builders frequently abandon them and Move to other locations.
4. Various molluscs, such as many of the numerous species of mussels, become Firmly attached to any convenient base by means of a mat of very strong chitinous Hairs. The tip o each hair becomes cemented to any suitable base, thus forming A dense mat on the surface, but these organisms have the power to loosen their hold-fasts and migrate to new locations.
   When they die, the mat of chitinous hairs remain firmly attached to the material Last occupied.

Motile Organisms.

This third group of organisms may influence the corrosion of metals in salt water, even though very indirectly. The constitute:

1. Some of the worms, particularly the scavenger varieties which leave mucilaginous excretions.
2. Mollusks, such as the sea slugs and snails.

The slimy film execreted by these animals may have little or no effect on a metal, but because of its consistency frequently smothers and rolls the more minute fouling organisms covered by it.

Film-Forming Organisms.

In addition to marine bacteria, large numbers of other unicellular marine organisms are usually among the first to appear on any material submerged in salt water. This film of microscopic organisms is of importance, principally because it may provide a favourable foothold for macro-organisms. It has been thought that if these micro-organisms could be prevented from becoming permanently attached, or the firmness of the attachment could be decreased, later fouling by the larger multicellular plants and animals would be greatly lessened or eliminated. Experiments show, however, that barnacles, at least, can become directly attached to the of a material without the aid of the microbiological film, although it is possible that such surface attachment of the larger fouling organisms is not so permanent as if it occurs on the organic film.
The appearance of a steel panel covered with various fouling organisms after immersion in sea water is shown in Fig. 1

Mud Tubes and Other Marine Organisms on Steel
Specimen 30 cm2 after immersion in sea water.

Distribution.

Fouling organisms are plentiful from the Artic Circle to the Antarctic.
Although they are many more kinds of organisms in the tropics, the bulk of growth in a given period of time may be as great in Labrador as at the Equator.
Most of the fouling organisms have very definite depths at which they survive of thrive.
Practically all true sessile fouling organisms live in comparatively shallow water.
Certain species of barnacles live at depths up to 60 meter, but these species thrive only at such depths and are rarely found attached to any objects near the surface of the water.
Other species of barnacles exist only in the vicinity of the high-water mark and are very rarely found at a depth of more than 1 meter below high water level.
Other organisms which inhabit this zone are the green algae, such as", "Enteromorpha which are commonly seen in the vicinity of the water line on vessels.
Fouling does not occur in the deep water off the coast because there are no objects upon which the organisms may secure the foothold necessary for their survival.

Factors Affecting Fouling.

Temperature.

Temperature is a very important factor in the life of marine organisms.
In northern waters the breeding season of most fouling organisms is restricted o the warmer summer months. Since fouling continues only to the end of the breeding season, it follows that most fouling occurs in northern waters only during the summer.
However, the organisms which do become attached during this period continue to thrive and increase in size indefinitely, dependent upon the length of life of the particular species involves.
In the warmer waters farther south, the breeding season is longer, until in the tropics it is almost continuous. Therefore, while a ship in the north may be completely free from fouling from November to June, in the tropics it might become badly fouled during any month of the year.

Effect of Ocean Currents and the Seasons.

A map referring only to the distribution of fouling has not yet been published.
For certain sections of the world, as for the coasts of Asia, the data are inadequate.
However, since the most important factor governing fouling distribution is temperature, distribution of marine organisms will probably agree closely with maps based on temperature.
Several such maps are combined in Fig. 2

(shaded tropical water is always above 20 C – heavy black coastal areas are regions of up welling cold bottom water)

The demarcations depend on the limits of empirically known critical maximum or minimum temperatures, localities in which the range of temperatures is exceptionally great, or places where there is a rapid transition from one to another set of conditions.
In no case will there be a complete change in the population.
But at any such point a sufficient number of organisms will find their limits of tolerance to give a distinctive character to the faunas of the two sides of the boundary.
The map (Fig. 2) shows a shaded tropical zone in which the water is always above 20 C (= 68 F)..
Outside of this is a subtropical zone with water still generally warm.
It is bounded by the temperate regions, outside of which in turn are the circumpolar cold waters. The greatest difficulties lie in localizing the boundaries in coastal waters, which are the most important in fouling considerations (the common fouling form is the mussel ("Mytilus edulis")
In practical terms these zones indicate roughly the regions in which similar types of fouling may be expected.
The composition of the fouling population is not the only feature dependent on temperature.
Fig. 3 shows the seasons of attachment of various fouling types at eight (8) different locations with varied temperature conditions. Most organisms in regions with cold waters part of the year do not breed continuously, but only at times when certain critical temperatures are attained.
Differential requirements in this respect result in the successions shown. Such differences are often found for separate species of the same group, as illustrated by the barnacles at Woods Hole (see Fig. 3).
Other cases are concealed in the graphs by temporal overlaps.

Seasons of Attachment of Various Types of Fouling at Eight (8) Locations.

A further point is the fact that for each species there are one or more peak periods of attachment, when it becomes especially abundant. These peaks characterize even the tropical fouling, in which, as at Madras and Hawaii, given species may be attaching to some extent throughout the year. Because thy are contingent in large part on critical temperatures for breeding, the peaks for different organisms do not necessarily coincide, but the great aggregate of them tends to occur in the warm months.

Motion.

Since fouling organisms must become attached to some base while still very minute, it is very difficult for them to secure a firm foothold on objects which are in motion.
On floating materials, in motion because of tide or current, it is conceivable that the larvae in the vicinity may be drifting at the same approximate speed and direction and hence have no difficulty in becoming attached.
The exact speed which would be too rapid for the various species of marine organisms to become attached has not been determined.
It appears to lie in the range of 3-to 6,5 kilometers per hour and is influenced by the roughness of the surface involved.

Color.

Many of the fouling organisms are affected by light.
The majority occur most plentifully on shaded, or dark, surfaces. The heaviest fouling is generally found on the northern side of stationary objects in the northern hemispheres.
This is true of mussels, hydroids, and many of the algae.

The green algae, such as “Enteromorpha”, thrive best in the light. In general, the lighter shades of protective coatings on submerged materials, the whites and light grays and yellow, are somewhat less subject to fouling than the darker shades, all other factors being equal.

Attachment of Fouling Organisms.

When in the minute larval or undeveloped juvenile form, the various fouling organisms secure the necessary permanent foothold in a number of different ways, each characteristic of a particular group. Many species of the algae, shortly after landing on a favourable surface, secure a firm attachment by exuding a mucilaginous material with hardens to a glue-like consistency. As the plant grows, root-like growths spread over the surface of the base, greatly increasing the firmness of attachment. A very similar method is used by the plant-like animals known as hydroids.
Other groups of fouling organisms, such as the barnacles and some of the molluscs, excrete a calcareous material which is deposited on any suitable submerged base to serve as a point of attachment.
With still others, the cementing material is of a siliceous nature.

Effect of Surface.

A hard, smooth surface generally provides a more secure footing for fouling organisms than a soft material.
The adherence on hard vulcanized rubber is much stronger than it is on soft rubber.
On a smooth polished surface of stainless steel a barnacle (=”Balanus Eburneus”) can obtain an exceptionally firm foothold. It is very difficult to remove such organisms even with metal scraping tools. This is also true to a somewhat lesser degree when these organisms land on glass.
On ordinary steel the firmness of attachment is much less. Similar effects are observed with protective coatings on metals.
Non anti-fouling paint coats with a hard glossy surface provide a firmer foothold for the organisms than softer paint films.

Effect of Corrosion Products.

The physical condition of a firm hard surface which provides an excellent base for fouling organisms may change after being submerged in salt water.
The initial growth on ordinary steel may be as great as on stainless steel, but corrosion products form very quickly on ordinary steel and the character of the surface is changed.
The organisms become fastened not to the metal, but to the surface of the film of corrosion products.
The firmness of foothold of the organisms is then equal only to the adhesion of the corrosion film. With a material such as stainless steel, where the corrosion-product film formed on the surface of the metal is negligible, a fouling organisms may be expected to maintain its foothold throughout its normal life.
With copper and certain high-copper alloys, the relationship between corrosion and fouling is very apparent. As compared with steel, these materials form corrosion products that are less voluminous, and a larger proportion is carried away either in solution or in suspension. In addition to any toxic effect, this continual loss or sloughing of corrosion products serves to prevent any prolonged attachment of fouling organisms. If the usual corrosion of copper or its alloys is arrested, as by galvanic action, the normal formation of corrosion products does not occur and fouling can then proceed as on other inert surfaces.

Effects of Encrusting Materials on Corrosion Physical Factors.

The first spot of cementing material enlarges as the animal grows.
With the oyster, the organic lime deposit may form a tightly adherent base which covers an area of several cm2.
If the base is equally adherent to a metal over the entire area, this base may be expected to protect against corrosion.
If the surface is uneven, and water penetrates, there will be different oxygen concentrations at points under the lime base and elsewhere on the surface of the metal.
Oxygen concentrations cells may then accelerate corrosion. This occurs with may of the fouling organisms, particularly with many of the numerous species of barnacles. It also may be caused by one or more micro-organisms, such as diatoms of “Foraminifera”, having become attached to a portion of the area over which the macro-organism grows.
Any uneven growth of micro-organisms on a portion of the metallic surface over which a macro-organism extends its base may result in unequal adherence of the latter.
Because of this unequal firmness of attachment beneath some portions of the base, oxygen concentration cells may develop, resulting in corrosion.

Chemical Factors.

Another entirely different and very important type of corrosion is encountered when, in the process of expansion of the base by growth, an organism completely surrounds and covers a later arrival, or smaller organism. The covered organism quickly dies.
Degeneration sets in, followed by the probable production of hydrogen sulphide. An acid condition results which causes accelerated corrosion.

Destruction of Protective Coatings.

Some organisms, particularly certain species of barnacles, such as “Balanus Eburneus”, are capable of penetrating or otherwise damaging protective coatings on metals. In the process of growth and the spreading out of the base of the organisms over the surface of any material there is also exerted a very strong downward pressure.
As a result of this pressure, the outer edge of the base may penetrate the film of protective coating. As the diameter of the base increases, the paint film is pushed up on the sides of the growing organism. In some of the thick bituminous enamels and tar coatings, the organisms may penetrate through approx. 6 mm of coating to the base metal, which subsequently becomes exposed to corrosion aggravated by its localization.
On a hard, dense, protective coating, penetration by these organisms is prevented, but in many cases the growing organisms become more firmly bonded to the protective coat than is the latter to the metal. When any action dislodges the organism, the complete paint system remains attached to the organism rather than to the metal.
Accelerated corrosion of the exposed metal follow.
It has been found, at least with some paint coats, that the difference in the filmness of adhesion of the paint coat beneath the base of an organism and that of the paint coat outside of, but adjacent to, the base of the organism, results in accelerated corrosion in the form of pits directly beneath the organism even while the paint system and the fouling organisms are apparently undisturbed. This may be the result of oxygen concentration cells having been formed beneath two adjacent areas, over one of which the paint coat is firmly adherent and at least somewhat impervious, whereas in the other paint coat, because of the action of the fouling organism, is not adherent.

Anti-Fouling Measures.

The problem of fouling of surfaces subjected to immersion in sea water has long been serious.
The major alleviative efforts to date have involved the use of an “anti-fouling paint”, applied in the too-often vain hope that, by its nature or content of toxic agents, fouling growths would be prevented or at least reasonably inhibited.
To this end an almost unlimited number of specific compositions, for which anti-fouling properties are claimed, appear in the patent and technical literature.
In many preparations the beneficial effect is attributed to the composition of the vehicle, in others, to the peculiar fashion in which the several ingredients are compounded together. In by far the greatest number, the virtue is ascribed to the presence of one or more poisons.
The phototropicity of certain types of fouling organisms has frequently been demonstrated by biological studies. The suggestion has therefore been made that color alone is the most significant factor in anti-fouling paint performance. The argument of light versus dark paints is still unsettled.
It has more recently been asserted that the only effective approach from the paint standpoint is to strive for extreme exfoliation or underwater chalking properties, but the relative merit of chalking coatings versus toxic coatings is still undetermined.

The Fouling Process.

The fouling of a ship’s hull, which begins as soon as the ship is water-borne, can be divided into three (3) phases taking place more or less simultaneously – the formation of the slimy micro-biological film – the attachment of macroscopic fouling organisms (always in larval form or almost always) – and their growth into the mature forms, visible as barnacles, molluscs, annelids, bryozoans, algae, and other fouling growths.
The probable role in the fouling process of the micro-biological film has been described before.
Experiments indicate that slime formation on anti-fouling paints may eventually vitiate effects of the paint by a simple blanketing action preventing lethal concentrations of the toxic agents from building up at the slime film-water interface.
Where sufficiently high toxic concentrations can be realized, in spite of the slime film, slime-covered surfaces may be maintained free from macro-growths for may months.
As discussed in the previous chapter, all the important macroscopic forms mature from tiny microscopic larvae. For a short time these larvae swim freely in the water.
Then, after a period varying from a few minutes to several weeks, depending upon the specific organism, they must become attached to a surface in order to survive.
After attachment, metamorphosis into the adult form and growth are very rapid. The effectiveness of anti-fouling paint depends upon its ability to hinder or prevent the primary attachment of the larvae. One attached; they grow regardless of the toxicity of the paints since the poisons have little or no effect on the adult organisms at concentrations attainable in the paint-water interface zone.
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Use of Paints
Anti-fouling Paint Formulation
Note: Important to the study of introduction of Impressed Current/or active/Anti-Fouling System “ICAFS”(Bright Spark b.v. – Joure)

With a few exceptions, every commercial anti-fouling paint carries copper in some form or other as the active toxicant. By far the major number of published formulas employ red cuprous oxide, alone or fortified with minor amounts of other toxic agents (arsenic

compounds). For the yachting trade the so-called racing bronzes, which employ metallic copper powders as the active pigment, have come into prominence.
It is now well established that the anti-fouling efficiency of a hull paint is substantially a linear function of the percentage of dissolvable toxic pigment carried in the dried paint film. The amount of toxic in a drum with paint – containing 4 liters, is a meaningless figure so far as predicting anti-fouling life is concerned, unless the total non-volatile content also is reported. The copper content of a representive group of commercial hull paints selected at random averaged 20-to 25% calculated as Cu_2O, (HgO was 3,5%, but not more allowed). Such paints seldom last longer than 6 months without fouling.
Researches carried out over a period of years (note: many of them unpublished for security reasons) have indicated that anti-fouling performance in excess of 5 - to 6 months demands copper concentrations approximating 2x the concentration found in most commercial paints.
At this toxic level, the advantageous effect of adding mercury compounds is no longer so apparent.

Toxic Properties of Metallic Copper versus Cuprous Oxide.

The effective soluble toxic complex/$CuCl_2$) – can be built up equally in the surface water interface zone from:
1) sheet copper
2) metallic copper powder
3) cuprous oxide
Or 4) other soluble and dissociable copper compounds.

That is, the toxic sources differ only in their ability to furnish the active toxic ions.
It is the soluble complex which has bio cidal properties.
Thus the primary toxicity of such a pigment is best measured by its available copper content.

* Cuprous compounds are effective because they dissolve to liberate cuprous ions.
* Cupric compounds are ineffective because they are insoluble in sea water.
* Metallic copper is effective because under most conditions it corrodes to yield the necessary cuprous ions.

Inhibition of Anti-Fouling Efficiency.

It is thus apparent that any factors influencing the primary rate of solution of the toxic agents will profoundly affect the performance of the anti-fouling paint. Typical of such factors is the nature of the binder employed in the paint.
If this contains substances capable of tight compound formation with cuprous ions, the life of the paint may be very short.
The blanketing effect of slime, with subsequent overgrowth of fouling organisms is an illustrative example. The slime film concentrates and holds the copper ions – precipitation takes place and fouling ensues.
One of the most serious causes of anti-fouling paint malfunctioning is attributable to accidental contact of this paint with the bare steel hull.
The mechanism probably involves the local deposition of copper by interaction with iron or steel, resulting in great depletion of the copper reservoir in the interface zone. The phenomenon is demonstrable with both metallic copper and cuprous oxide paints.
For this reason the importance of having adequate primer coats on steel hulls before applying the anti-fouling paint cannot be exaggerated.

Alternative Anti-Fouling Pigments.

The technical literature recites numerous compounds to which anti-fouling activity has been assigned.

Typical are
- copper resonates
- copper arsenite
- calomel
- copper oxychloride
- basic copper carbonate
- selenium oxide
- copper and zinc selenides
- cuprous cyanide

And numerous arsenic compounds.

In addition, a wide variety of organic compounds have been described and patented as anti-fouling toxicants.
The use of certain metallo-organic complexes has been widely explored in recent years.
In general, it can be stated of these alternative pigments that few if any are as effective on a "pound-for pound" basis as a simple copper scale, copper, or cuprous oxide, and non can presently compete on a "cost-per-pound" per month of effective paint life.

Other Measures
Use of Electric Currents

As we know numerous investigators have suggested the possibility of applying either DC- or AC current to the hull at intermittent intervals, to prevent primary attachment.

* The larval forms of most fouling organisms are remarkably insensitive to DC-current without intervals.
  High-frequency AC-current has also been employed on an experimental scale, with little success to date.
* Anti-Fouling System by impressed DC-current with intervals is the ultimate solution, to avoid deposition of calcium, magnesium, and strontium basic salts as an adherent film (appears to be a limiting factor).

Theory of Anti-Fouling.

Anti-fouling paints (for instance hull-protection of vessels, water inlet systems, etc.) are active when leaching rates of copper oxide exceed 10 microgram/cm2 per day, which means that a surface of 1 m2 can be kept clear of biological growth by leaching of approximately 30 gr. of copper oxide/year.

Marine Fouling/Automatic Electrolytic
Fouling Prevention.

This is an automatic electrolytic process for the prevention of fouling by growth of wiry type algae, shellfish, mussels, coral and barnacles.
The system is based on the same principle as the use of marine anti-fouling paints where copper pigments are used for provision of a toxic medium.
It is established that cuprous oxide leached from the paints has a strong toxic action on growth such as algae, shellfish, barnacles and other growth.
Similar amounts of copper oxide are active in our "BS-System".
Whereas anti-fouling paints are only active during the period the leaching rate is over the given quantity, in our "BS-System" cuprous oxides are formed continuously in controlled

amounts and similarly the action against growth and developments of algae and shellfish, etc. is continuous and controlled.
It would appear that the use of electrolytic red copper as anodes only could have dangerous consequences.
Corrosion cells can be established when dissolved copper is displaced from solution and redeposited on steel surfaces.
However, this possibility does NOT and CANNOT occur in the conditions of use since in the first instance the quantities of copper going into solution are negligibly small and secondly this copper does NOT remain as dissolved copper, but is immediately oxidized to copper oxides, which are insoluble.
Both cuprous and cupric oxides are insoluble so that the amount of copper ions in water is untraceable and far below so called natural levels.
For environmental reasons Aluminium Anodes can be used in combination with Copper Anodes, because direct current (= DC) dissolution of aluminium alloys results in formation of “colloidal” solutions and hydrated aluminium oxides or “floc” which is gelatinous and encapsulates the precipitated copper oxides so that they are removed as a sludge.
Similarly, “suspended” impurities in the water are removed so that cleaner water is produced.

Example.

The quantities of copper forced into solution are relatively small for example a water inlet of 600 m3/hour, we dissolve only 80 kg of copper per year, and that means less than 0,02 ppm or mg/kg of which most of the copper is precipitated and 20 kg of aluminium per year.

Designs of Automatic Anti-Fouling System are based on type of:
- water
- flow rates
- conditions and fouling character

but the amounts of copper (Cu) and aluminium (Al) dissolved will be of this relative magnitude.
All immersed steelwork via electrolyte connected to the Cu-and Al-anodes will be fully cathodically protected and the corrosion rate of allied pipe work down stream reduced by reduction of dissolved oxygen in solutions and the formation of mixed Fe-Al-oxide crystals at the steel/pipe surface.

Advantages.

- The system as disigned and developed by us, Bright Spark, can be regarded as a perfectly safe system.
  Not only on account of the corrosion dangers, but it will not create any danger for handling personnel, nor will it give any pollution effect in the effluent.

- The system will need little care and maintenance and with the exception of replacement of worn anodes (once a year as minimal), will work fully automatically.

- The system is cheap. Running costs are low, low consumption since the system works at very low voltage.

Consequently the major running costs are in the replacement of the copper and aluminium anode(s) which costs are very low in comparison with systems which depend on addition of chloride or other chemicals.