PART II

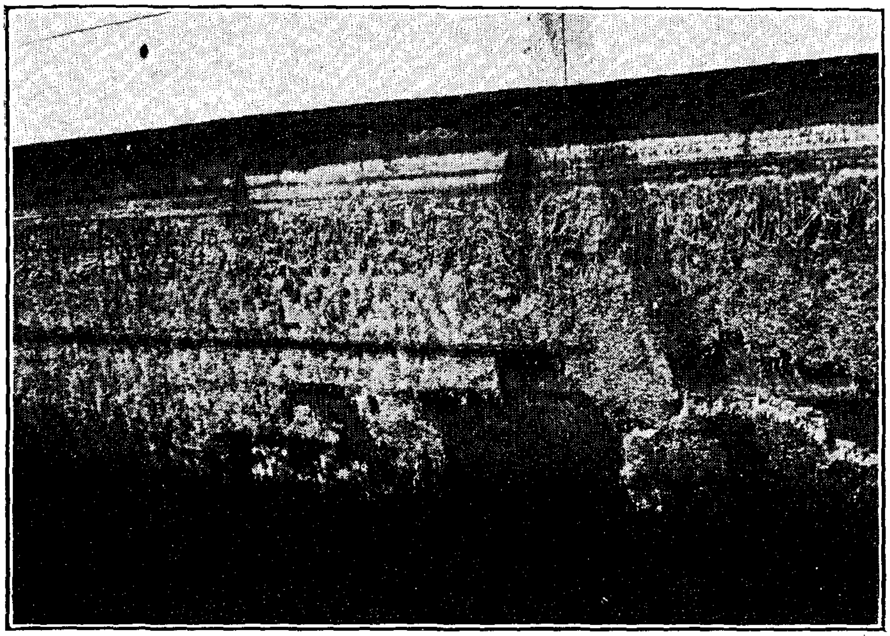

FIG. 1.—PORTION OF PORT SIDE OF H.M.S. "SIRIUS" SHOWING HEAVY GROWTH OF TUBEWORMS AFTER A PERIOD OF SERVICE IN THE MEDITERRANEAN

BIOLOGY OF THE UNDERWATER FOULING OF SHIPS' HULLS

by

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TYPES OF FOULING ORGANISMS

The organisms capable of settling on the outer bottom of ships and causing fouling comprise an assemblage of more or less lowly animal and plant species derived for the most part, from the coastal regions of the seas of the world. The natural habitat of most of these species is the intertidal zone and the sea-bottom to a depth of perhaps 20 fathoms. In this zone, nearly all live attached to rocks, to the larger hardshelled animals and to the larger seaweeds. Inevitably they colonise any structure introduced by man unless this is adequately protected. Thus breakwaters, piers anchors and submerged ropes and, most important from the economic standpoint, the outer bottoms of vessels may rapidly be covered by a variety of these organisms. Because they are essentially inshore or neritic species, they tend to be rare away from the land and a vessel rarely receives its quota of fouling species while on the high seas. It is on entering inshore waters and especially when alongside or at anchor, that settlement of fouling organisms occurs.

There is no uniformity of distribution of fouling species in coastal regions. It is, of course, well known that some ports are exceptionally bad from the fouling standpoint whilst others are good and "scouring" ports may even cause cleaning of a fouled bottom through the abrasive action of suspended silt.

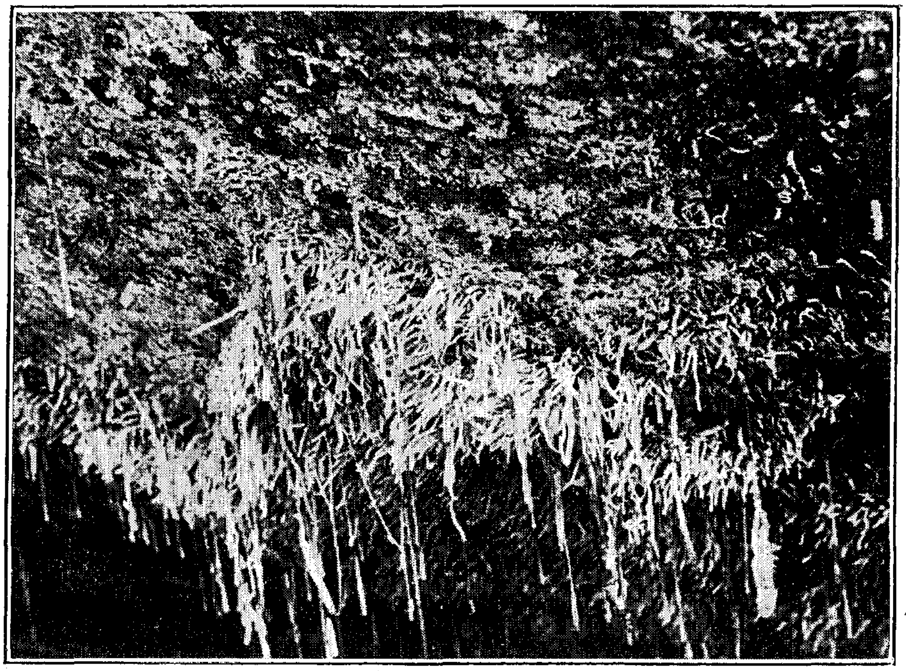


FIG. 2.—" CLOSE-UP " OF TUBEWORM FOULING ABAFT THE OUTER PORT PROPELLER OF H.M.S. " SIRIUS "

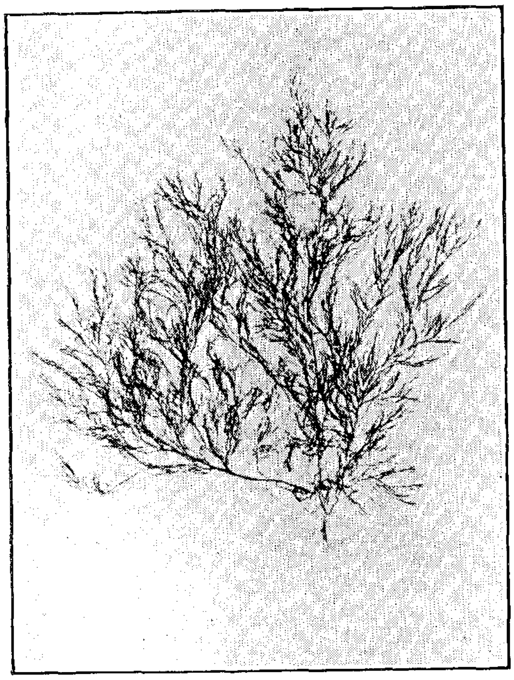
Density of occurrence of species is generally highest in tropical and subtropical waters whilst fewer organisms occur in higher latitudes and very few in polar seas. There is a general similarity between the types of fouling experienced in different parts of the world, because the groups of animals and plants concerned are world-wide in their distribution. Locally, however, one or more may be predominant.

Thus, exceptional growths of tubeworms (" coral ") may develop on ships in Mediterranean waters (Figs. 1 and 2). There are, however, considerable specific differences between the fouling types from different regions. Green, brown, and red algae (seaweeds) foul ships in all parts of the world but the species settling on a ship in U.K. waters, will be mainly different from those settling in a West African port and again both will be distinct from those settling at, say, Singapore. Similar differences exist between the barnacles, tubeworms, and other animal growths causing fouling in different parts of the world.

The various types of seaweeds and animals causing fouling have been outlined and illustrated in the booklet " Fouling of Ships' Bottoms : Identification of Marine Growths " by the Marine Corrosion Sub Committee of the Iron and Steel Institute and distributed by Admiralty to H.M. Ships. The genera and species mentioned there occur in British waters but closely allied types are found in all seas. Four species of British seaweeds are shown in Fig. 3. It will not be necessary to describe these forms afresh and this paper will attempt to indicate some of the biological and physical factors affecting settlement of fouling organisms and to outline the methods of preventing fouling and the work that is being done on the subject.

Occurrence and Settlement of Species

The geographical distribution of fouling species has been stated to be practically world wide. If the distribution in time is considered, a different picture is



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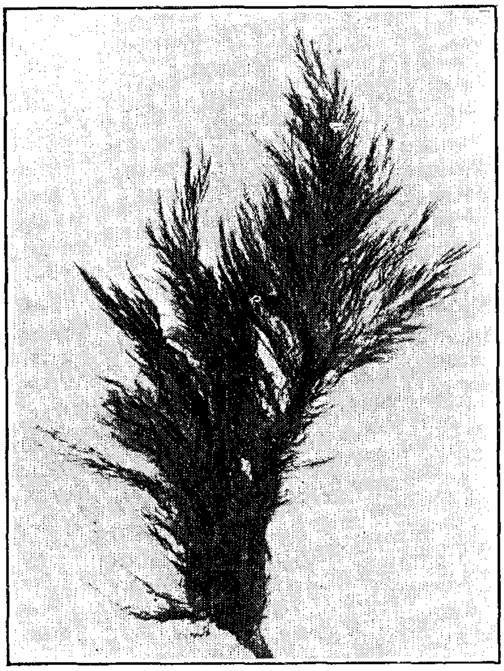

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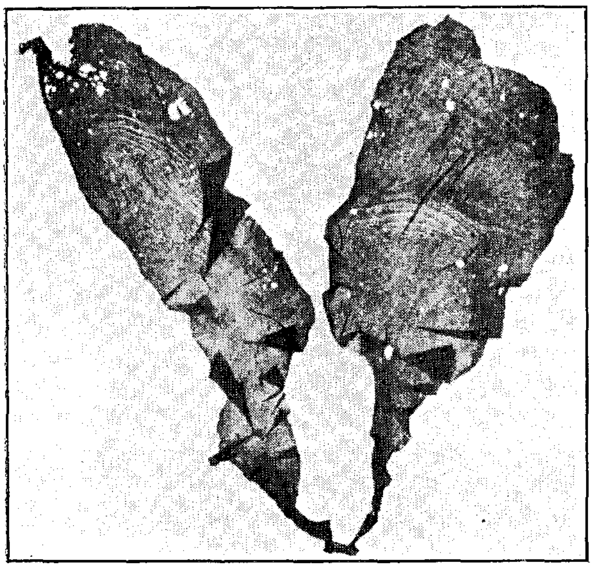

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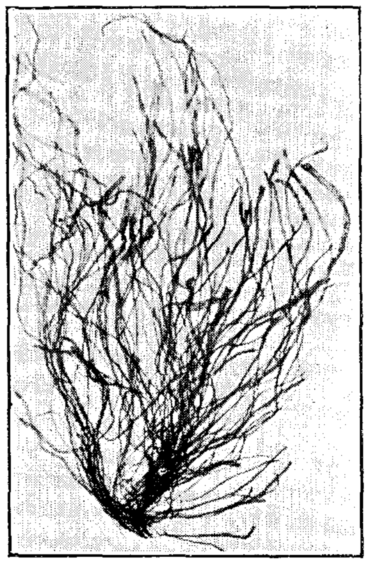

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FIG. 3.—FOUR SPECIES OF COMMON FOULING SEAWEEDS :

(*a*) CERAMIUM, ONE OF THE FEW COMMON RED SEAWEEDS (USUALLY PURPLISH IN COLOUR) FOUND ON SHIPS

(*b*) ECTOCARPUS, A FINELY BRANCHED BROWN SEAWEED

(*c*) THE SEA-LETTUCE (ULVA), ANOTHER COMMON GREEN SEAWEED

(*d*) ENTEROMORPHA : THIS IS THE COMMONEST GREEN SEAWEED COMPONENT OF THE " GRASSLINE "

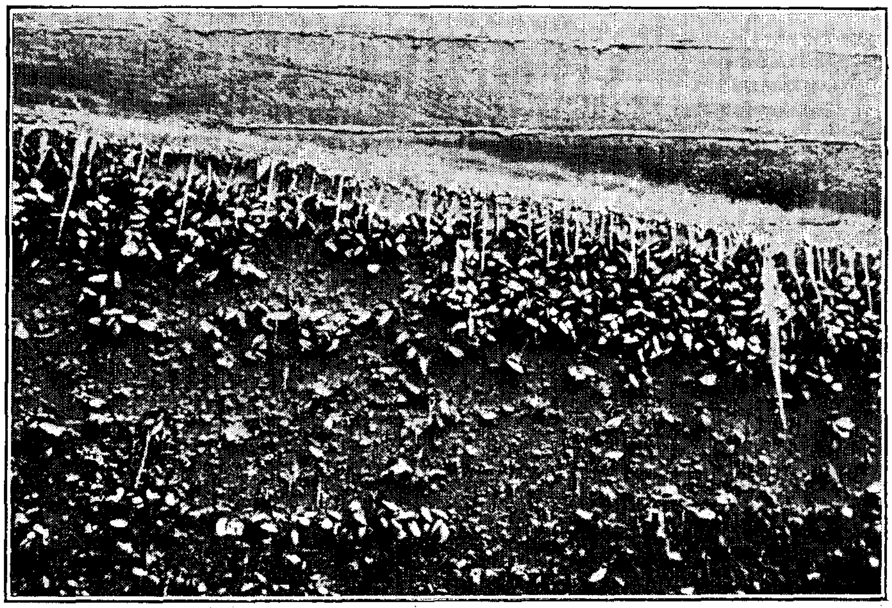

FIG. 4.—WATERLINE FOULING ON TIMBERS OF R.R.S. " RESEARCH." THE FOULING AT WATER LEVEL CONSISTS OF NARROW BANDS OF A RED ALGA (BANGIA), YOUNG ENTEROMORPHA AND LONG FRONDS OF THE BROWN OAR-WEED (LAMINARIA). FOULING AT ALL LOWER LEVELS IS MAINLY THE EDIBLE MUSSEL AND A FEW BARNACLES

obtained. In tropical waters, many species of tubeworms and barnacles and probably some seaweeds may breed throughout the year. Thus young settling individuals of these species are present at all seasons, searching for a suitable place to attach themselves. To take one case only ; on the Florida coast barnacles settle during most months of the year and it is doubtful if the settling stages are ever entirely absent. There is a peak period for settlements, lasting for most of the summer months, followed by a short ' winter ' period when fewer larvae are present. In contrast, barnacles breed in this country during fairly well defined periods, in the spring and again in late summer or early autumn. In the English Channel there is a very sudden appearance of young newly settled barnacles in late March and April and another fairly heavy settlement occurs in August-September. Relatively few settle at other seasons of the year. Similar ' seasons ' occur for most if not all fouling species in British waters.

From this fact alone it is clear that the particular fouling appearing on a ship at any place will depend upon the time of the year, controlling the presence of settling organisms. Further the numbers present may vary very considerably. The experience of several investigators working on fouling in the U.K. is that there are " good " and " bad " seasons for, say, barnacles. The factors governing these "good" or "bad" seasons are not easy to ascertain but from general considerations, it appears they are related to the physical and chemical condition of the waters and to the food supply. The former affect the reproduction of the microscopic plant forms of the sea e.g., low light intensity and low phosphate or nitrate content will all tend to reduce the microscopic flora of the waters. The food shortage so produced will seriously affect the production of young barnacles because during the period from egg to settlement they undergo a free-floating larval existence when they are dependent on micro-organisms for food. For further details on the relationships between the abundance of marine organisms and food supply, the reader should consult the various text books of marine biology and oceanography where the subject is dealt with more fully than is possible here.

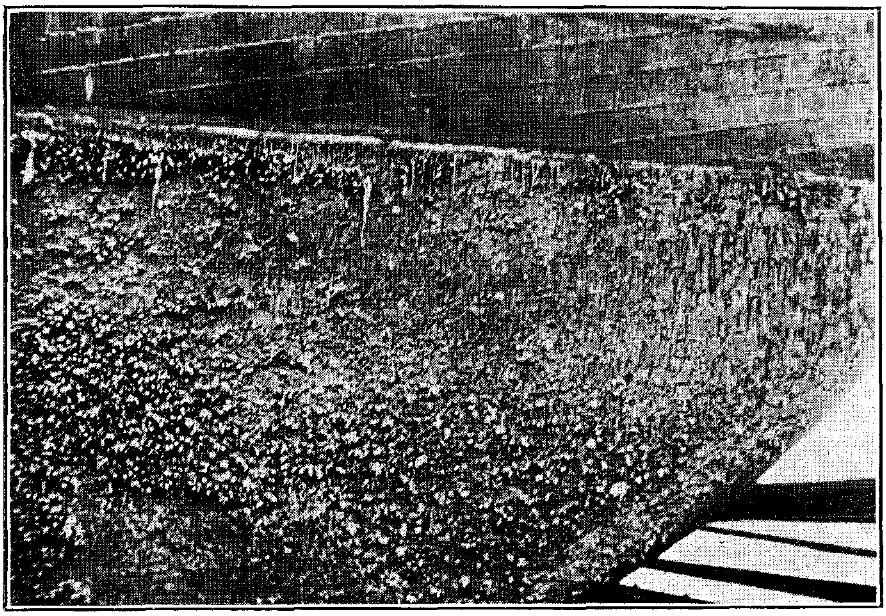

FIG. 5.—FOULING ON THE BOWS OF " RESEARCH." RED SEAWEEDS OCCURRED HERE AS MUCH AS 3-4 FEET BELOW THE SURFACE, PROBABLY BECAUSE OF THE GREATER ILLUMINATION DUE TO LACK OF CURVATURE OF THE HULL

The places in which the young organisms settle are also conditioned by a number of factors. Broadly speaking, plants seek the light which is necessary for their metabolic processes (photosynthesis) whereas animals, not so dependant seek the less well illuminated regions. This is the reason for the concentration of algae at the waterline of ships—forming the " grass-line " on a foul bottom (Fig. 4). Closer inspection of the waterline and below on a fouled hull will show that mixed with and below the green belt are a number of brownish seaweeds and below these (very seldom in the green zone) occur reddish seaweeds (Fig. 5). This distribution is precisely similar to that found on a shelving shore where green species occur near high water mark, brown ones at half tide and red seaweeds only near and below low water mark. On the lower parts of the hull, a few red weeds may be found, but fouling here and on the bottom flats is almost entirely of an animal nature.

Given a structure suitable for settlement, many of the animal species appear to exercise some degree of " choice " as to where they attach. Crevices are quickly colonised as these give protection from the flow of water and from enemies. The lee-side of projections, e.g., a rivet head or the faying edge of a plate, are also readily colonised. When suitable sites are limited, settlement appears to be more general and any area not covered by other species may be colonised. In times of heavy competition, e.g., at the height of the barnacle settling season, these animals have even been known to settle on highly toxic experimental paint surfaces for want of better places. The result can be most striking a month or so later when all around on innocuous surfaces there is a heavy barnacle growth whilst the toxic surfaces are bare and clean, the young barnacles having been poisoned and their insecurely attached, weak shells, having fallen off.

The quantity and kind of fouling occurring on a vessel clearly depends upon the interaction of a number of factors. The ports and anchorages visited and the time of year will determine broadly what species of organisms are potential settlers. The extent of fouling will be conditioned by the degree of success in breeding of these organisms, to the extent of there being virtually no larvae

FIG. 6.—A TEST PANEL EXPOSED ON A RAFT IN THE MENAI STRAITS, CAERNARVON, FOR 10 MONTHS. THE PAINT HAS WORN THIN IN THE BRUSH MARKS AND ALGAE HAVE GROWN IN THE LOCALLY NON-TOXIC " TROUGHS "

of any one species, or so many, that they may completely cover any suitable, or even unsuitable, surfaces. Finally, fouling will depend upon the precise condition of the outer bottom paint. If this is *efficient*, there may be no settlement at all, or the few organisms that settle will soon die and drop off. The first places to foul on an otherwise flat paint surface, are the marks left by the brush in laying off the paint. These marks are really minute " troughs " in the paint film where the film is thinner than over adjacent areas. These thin troughs lose their toxicity before the thicker parts of the paint film and fouling can develop on them. Fig. 6 shows a raft test panel after ten months immersion on which various green algae have settled over the vertical brush marks. This phenomenon also illustrates the value of a thick anti-fouling coating. In raft trials, several months extra life have been obtained by applying a second coat of anti-fouling paint to a test panel.

It is clearly at this point—the period of settlement—that the problem of ship-fouling is best attacked. The small, relatively unprotected larval stages will be more easily poisoned than the adults, owing to the greater permeability of the surface and the nearness of the whole body surface to the poison dissolving out from the paint. Secondly, the adult organisms stand up some distance from the paint surface, and are bathed in part in a less toxic medium, whilst their basal parts may be protected by a thick layer of calcium carbonate. Thirdly, the period of metamorphosis (change from the free swimming larval stage to a very different attached adult) is frequently a critical period in the life history, when the mortality rate is naturally higher. Fourthly, it may be possible to upset the chemistry of the attaching mechanism, though at present

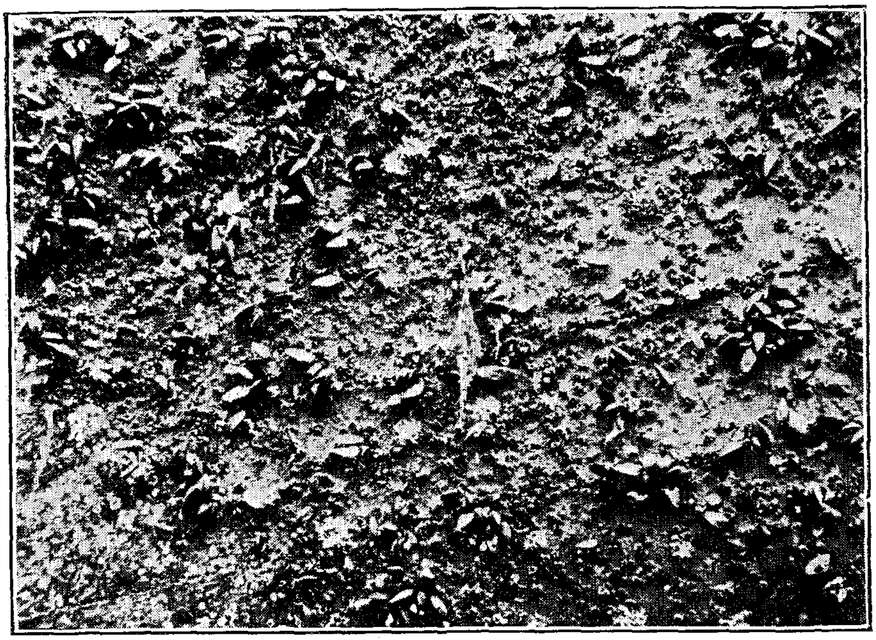

FIG. 7.—PORTION OF A HULL SHOWING DEAD BUT FIRMLY ADHERENT BARNACLES AND CLUSTERS OF MUSSELS

we know very little about this process, except that it appears to be a kind of "tanning" of an adhesive substance similar to the tanning of hides. Fifthly, it is of less value to kill the adult organism as in many cases, *e.g.*, barnacles or calcareous worms, the hard skeletons remain firmly attached long after the animal is dead.

Prevention of settlement of Organisms

The time-honoured method has been to coat the outer bottom with some material or mixture of materials that would discourage settlement or poison such organisms as did settle. Present-day anti-fouling paints are based on this principle, to which end they contain substances known to be toxic to marine life. On the average, anti-fouling paints contain up to 25% of copper as cuprous oxide with or without a small amount (up to 7%) of mercury as mercuric oxide. Other copper or mercury compounds are sometimes used, notably metallic "flake" or "leaf" copper. These latter have been experimented with extensively in the U.S.A. Both copper and mercury in solution are very toxic to marine animals and plants. Less than 1 p.p.m. (parts per million) of copper is lethal to a large variety of plant and animal organisms. Mercury appears to be more toxic than copper to animals but less toxic to plants.

A few organic compounds such as the thiuram disulphides have been used with varying success in anti-fouling paints. The "war gas" D.M. (chlorphenarsazine) and derivatives, have been used experimentally with some success, and it is believed that this or an allied substance is being used by a section of the industry.

The poisonous pigments are incorporated in the paint medium and the essential problem in formulating an anti-fouling paint is to incorporate the poisons in such a manner that they are available in lethal quantities and yet are not lost at an excessive rate, which would merely have the effect of unnecessarily shortening the effective life of the paint film and be uneconomic. At the same time the paint film must remain intact, and wear at an even rate so that non-poisonous areas do not develop through excessive local losses. To obtain solution of the poisonous pigments, the paint must be permeable to water while yet remaining firmly adherent to the hull. It is further desirable that the anti-fouling effect should extend over a small area at the margin of the paint film, so that small areas where the paint has been removed mechanically may still be kept free from fouling. The anti-fouling composition should be non-corrosive, or nearly so. In practice, these compositions tend to accelerate corrosion slightly, due to the action of the contained cuprous oxide, and protective (anti-corrosive) undercoats are necessary.

These somewhat conflicting requirements have necessitated considerable investigation in the past and are still the subject of active inquiry. They are without doubt, the cause of the short life of many compositions that have been used in the past ; a paint that stands up well to water movement may liberate the contained poisons at too slow a rate and consequently foul badly. One that is an efficient anti-fouling agent may, on the other hand, erode so fast as to lead to a rapid breakdown of the film, leaving bare patches that foul readily. Furthermore, it is evident from trials of many different compositions that some anti-fouling paints require a few days soaking before they become fully effective against fouling, presumably because the paint film requires an initial period in which to absorb water before effective leaching out of the poison commences. A ship newly painted with such a composition and meeting a heavy barnacle settlement soon after undocking, may well foul heavily. Once well-established, the barnacles will be able to withstand any subsequent liberation of poison from the paint and persist, though no other colonisation may take place. Such very early settlements, depending upon the chance presence of the settling organisms at the time of undocking, probably account for the unexpectedly short life sometimes experienced with an anti-fouling composition usually regarded as good. It follows that a *new* coat of anti-fouling composition is not necessarily synonymous with an *effective* coat.

THEORIES OF MODE OF ACTION OF ANTI-FOULING PAINT

Three theories have been advanced to explain the mode of action of an anti-fouling paint and it would seem highly probable that each contributes towards the efficient action of at least some paints. It is most unlikely that the many anti-fouling paints now made, often very divergent in composition, all function in precisely the same manner.

Chalking Theory

The simplest explanation of the mode of action of an anti-fouling paint may be termed the " Chalking Theory." In this view it is the steady " chalking " or disintegration of the paint surface that is the protective principle. An unstable surface is presented to a larva seeking a place to settle. If it settles the surface beneath it will shortly disintegrate and the organism will become detached. This has frequently been noticed in raft trials to happen to quite large barnacles which have become detached solely through the chalking of the paint surface. Under service conditions they would probably have become detached sooner owing to the greater water pressure on them whilst the ship was steaming. It is unlikely that a paint depending upon this principle alone for its efficiency would have any length of life as the rate of disintegration would need to be high and the film would soon be broken down unless very thick, when the economic factor would arise. In practise no paints rely on chalking alone ; they all contain some poisonous principle. Chalking, however, certainly assists the proper functioning of these paints.

Sponge Theory

A second theory may be termed the "SPONGE THEORY." The paint film is visualised as a sponge formed of the solidified paint vehicle or medium in the interstices of which lie the insoluble (in the paint medium) particles of poisonous pigment. Water is absorbed into the paint film and a portion of the poison pigment goes into solution. This dissolved poison is thus held in the pores of the matrix "sponge" and remains there owing to the slow rate of diffusion possible from the film. The view is held that this contained dissolved poison deters the searching larvae when they attempt to settle and they do not attach to the paint film. This effect on the living organism is probably correct under some circumstances though there are conditions under which organisms appear to attach regardless of the poison.

If the paint matrix is soluble or erodible, the deeper lying particles are gradually exposed to the solvent action of the seawater and the concentration of poison in the interstices of the film is maintained, as long as there is any solid poison left in the gradually disappearing paint film.

If, however, an insoluble paint matrix, *e.g.*, a synthetic resin, is employed, only those particles will be dissolved which lie at the surface of the paint film. Once these have been dissolved and the soluble poison diffused out from the pores, the paint may become non-toxic. This will occur unless there is a sufficiently high toxic pigment content present for the particles to be in continuous contact. Under such conditions the deeper lying particles are attacked as the outer ones are removed and the film gradually becomes a matrix sponge containing a saturated solution in seawater of the toxic principle. The amount of toxic pigment required to make such a paint effective may be as high as 80% of the paint and clearly only a very tough vehicle will be able to form a durable film under these conditions. Considerable experimental work has been done on this type of paint, with a high pigment content and insoluble vehicle, but as yet they are not in general use.

A drawback to this "sponge" theory as an explanation of the mode of action of an anti-fouling paint, is that it does not allow for the continuous and sometimes high loss of poison from the paint film ; far more than could be accounted for by diffusion alone. Neither does it require the steady breakdown or "chalking" of the film that is so constant a feature of nearly all types of anti-fouling compositions.

Leaching Rate Theory

The third or "LEACHING RATE THEORY" endeavours to incorporate all of the observed phenomena shown by the paint film. This theory holds that an efficient anti-fouling paint must lose poison by leaching or solution, into the seawater at a definite minimum rate ; this rate being such as to create a concentration of poison at the paint surface sufficient to deter would-be settlers or to kill such as persist in settling. This theory is widely held in the U.S.A. and a rate of loss of copper from the paint film of 10 mgm/1,000 cm^2 of paint surface/day, is stated to be effective. Work carried out in this country by R.N.S.S. staff for the Admiralty Corrosion Committee and by the Marine Corrosion Committee of the Iron and Steel Institute is in general agreement with this quantity. Much work has been done on paint formulation in attempts to obtain and maintain such a rate for long periods. Increasing the cuprous oxide content of the paint has been shown (*a*) to increase the initial rate of loss, and (*b*) within limits to prolong the duration of an effective leaching rate.

A certain amount of work has been published by various American workers on the leaching behaviour of a great variety of experimental compositions and it is clear that the type of vehicle as well as the pigment content has a considerable bearing upon both the initial and subsequent leaching rate of a paint.

The interaction of the rosin or the resin-modified synthetic vehicle with the cuprous oxide pigment, is another factor of importance. Copper abietate or " rosinate " is formed and appears as a green solution in the paint solvent in cans which have stood for some time. Copper abietate is not very soluble in seawater though readily so in organic liquids and so copper converted into this compound may be rendered inactive as a poison. Alterations in the vehicle components or even in the " reaction time " in the preparation of the vehicle, may completely alter the behaviour of a composition. What was an excellent anti-fouling paint may become practically useless, unless such factors are carefully controlled.

The attraction of the " leaching rate theory " lies in the possibility of measuring the effective principle—the Leaching Rate—and methods have been devised for this purpose. Further, it is possible to correlate the measured leaching rate at different times in the " life " of an immersed paint film with the observed anti-fouling life obtained in raft exposures. Provided that the conditions of experiment are known and carefully controlled, the observed life of exposure panels is in reasonably good agreement with the age at which the leaching rate falls below the effective limit of 10 micrograms/sq. cm/day.

The principles entailed in both the " chalking " theory and " sponge " theory, can be regarded as secondary factors assisting in the maintainance of the leaching rate. " Chalking " of the film removes the outer exhausted portion, thereby exposing further particles of cuprous oxide to the solvent action of seawater. The " sponge " theory offers an explanation of how an adequate leaching rate can be maintained from a paint with insoluble matrix, provided that the pigment/vehicle ratio is high enough.

In practice, it would appear that all three suggested modes of action play some part in the efficient action of an anti-fouling paint. The greater importance of one method over the others probably depends upon the particular composition or type of composition under consideration. It is abundantly clear that the anti-fouling process is an extremely complex chemical system, of which many of the important details are at present unknown. There are even indications, from a number of effective paints, that leaching rate is not the essential factor in preventing fouling, but it is at present too early to speculate on this aspect. Meanwhile, the leaching rate offers a reasonable explanation of how the paint works and a method of estimating its efficiency.

Investigation of the rate of loss of copper and/or mercury (" leaching rate ") of anti-fouling compositions has thrown light on the reasons for failure of many experimental formulations both in this country and in the U.S.A. and may well become a generally accepted tool in anti-fouling paint testing. The method has the advantage that tests can be carried out on quite small painted panels and so effects an economy in materials and space as compared with raft exposure tests or service trials. These latter need only be done on those compositions that give promising leaching results.

As, however, no static tests, whether in the laboratory or on a moored exposure raft can duplicate actual service conditions, all three modes of testing are still necessary. Only the best need be selected for service testing and so much expensive and unprofitable testing on a large scale can be eliminated.

Whether a particular coating will foul or not is always dependent upon the living population of the sea present at the moment. There can be no absolute answer to the question of how long any paint will be effective. We cannot, in short, control the occurrence or abundance of the species of marine animals and plants that find a ship's hull a more or less desirable site on which to squat. Our aim must be to ensure that the anti-fouling composition is at all times capable of preventing the attachment and growth of those species capable of affecting appreciably the frictional resistance of the hull.