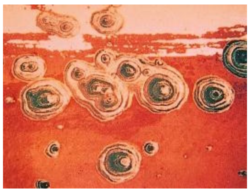
Corrosion

Corrosion is a natural reaction where steel under the influence of water and air transforms to rust. The speed of corrosion is enhanced by the presence of salt. A closer look at corrosion reveals an electrochemical process requiring a flow of current between surfaces having a difference in potential. These electrical potential differences on steel surfaces arise from a variety of causes such as the presence or absence of mill scale and/or local differences in the composition or treatment of steel. In a so-called corrosion cell differences in electrical potential exist between the scale free areas that become anodic and the scale covered areas that become cathodic. The electrons generated by the potential difference flow from anode towards cathode. Corrosion then takes place at the anode while at the cathode there is little or no corrosion at all. Initial products from anodic and cathodic sites are ferrous- and hydroxyl ions respectively. These ions diffuse from the surface and react to form ferrous hydroxide, $Fe(OH)_2$, which in turn is oxidised by dissolved oxygen to form ferric oxide, Fe_2O_3 (rust).

Corrosion can also occur when steel comes in contact with corrosive chemicals even when at first sight this is not expected. For instance coal in its basic form is harmless but coal ore may contain sulphur impurities, which in combination with moisture forms sulphuric acid, a strong corrosive chemical.

Another type of corrosion that deserves mention is biological corrosion caused by organisms such as the sulphate reducing bacteria (SRB). SRB are widespread over the world and start growing when conditions become favourable, especially when oxygen is absent. Such conditions can be found on submerged- or buried structures but also in water ballast tanks where often a layer of mud is deposited on the steel. The exact process has not been elucidated yet but basically SRB use sulphate as their source of oxygen and in turn produce sulphide ions. Sulphide ions are highly corrosive and as result steel corrodes to typical terrace-shaped craters with black iron sulphide on the crater bottom.



In seawater, the corrosion rate of unpainted steel is quite low, 50-175 micron per year, and corrosion is only dangerous when accelerated. The danger arises from the presence of cathodes whose area is large relative to the anodic areas - the conditions are then right for a high current density at the anodes and rapid metal loss (i.e. pitting). Chemical- and biological corrosion are two good examples of such conditions. Pitting is the most dangerous form of corrosion, because in its worst form it might cause total breakdown of the steel structure.

Corrosion in open air is dependent on the location and the climate. For instance, a constant high level of relative humidity has more corrosive effect than rainfall in less humid climates.
Air pollution, especially sulfur dioxide (“acid rain”) even has greater influence on corrosion. ISO 12944 distinguishes the following Corrosive conditions.

Table 1. Classification of corrosive environments according to ISO 12944.

Corrosive Condition		**Description of environment.**
C1	Very low	
C2	Low	Rural areas. Corrosive conditions are determined by humidity, precipitation and UV-radiation. Low level of pollution.
C3	Medium	Industrial areas with moderate air pollution. Coastal areas with low salinity.
C4	High	Industrial and coastal areas with moderate salinity.
C5	Very high	Industrial areas with a high level of humidity combined with severe air pollution. Coastal and Offshore areas with high salinity

By now it will be clear that protecting steel against corrosion requires a strategy where factors as steel exposure conditions and intended functional use of steel structures have to be considered.

Introduction to paints.

The most widespread method to protect steel against corrosion is the application of paints, because, having the same efficiency as other more complicated methods, this is easier.
Basically, paints are made up of solid particles dispersed in a fluid. When the mixed product is applied to the surface, the fluid dries up and binds the solid particles in a coherent film.
To this simplistic definition, we must add that the formulation of sophisticated paints used today in the protection of steel against corrosion is quite complicated; the right ratios, the properties of each component and the preparation methods have to be studied and scrupulously respected, because even the smallest variation can jeopardize the quality of the paint.
The main components in paint are binders, pigments, extenders, solvents and additives.

Binders.

The fluid part has the task of "binding" the solid particles as it dries up. Natural oils, such as linseed oil have been used as binders for centuries even though they have some drawbacks.
But for over fifty years, with the development of the polymers' technique, synthetic binders have been produced, and at present synthetic materials are used, at least partly, in all paints. This innovation has started an important evolution in the field of anti corrosion protection and the consequent advancement of the technologies in the production of paints. Synthetic binders are resins, such as for instance alkyd-, epoxy-, urethane-resins, each with different properties. In most cases, they are the most important constituents of a paint, and greatly contribute in giving them its required mechanical and physical qualities.

Pigments.

Colour pigments give the dry film opacity and colour.
Functional pigments determine the role of the paint in the system. It can give enhance properties such as hardness or resistance against abrasion, impermeability and protection from UV radiation. In addition, anticorrosive pigments such as zinc dust play an active role in prevention steel from rusting.
Extenders are the other solid components of a paint that are made up of substances that have a different chemical nature, grain-size and shape. Carefully chosen and mixed, they may be used to change a paint's consistency for application purposes, reinforce the film's mechanical and chemical strength and also to increase its hardness, its flexibility and its resistance against abrasion.

Solvents.

These are volatile organic compounds used to give paints the necessary viscous properties both in store and during the application, and also to regulate the film's formation time in the drying stage.
The correct balance between viscosity and volatility should always be found in order to be able to choose a solvent that in a given paint develops the above mentioned functions and that reduces the formation of pigment deposits on the bottom of the container during the application; for this reason, the solvent is often a pondered mix of several products, fit for use in temperate environmental conditions. When the paint is to be used, for instance, in torrid or polar climates, mix modifications might be necessary.
The content of the solvent in the paints varies a lot and some products are even totally solvent-free.
The technical sheets suggest the opportunity of adding thinners when using them, also indicating the type and ratio. Quite often a wrong thinning may lead to unsatisfactory results or problems in the application.
In fact, the solvent's evaporation speed from the drying paint film can affect the final properties of the painting. Generally, this speed is high in the first drying phase, but reduces in a second phase because of the solvent's property to spread among the molecules of the binder. A slow evaporation may cause the entanglement of the solvent in the film. A quick evaporation may cause other defects.
This is why one should use a minimum amount of solvent, which allows a satisfactory application and the realization of the required thickness.

Additives.

These are compounds of different types, which are often added as 'pepper and salt' to the paint for different purposes, for instance to prevent the formation of skins on the product surface in the container or as thixotropic agents to limit the tendency to sagging etc.

The classification of paints.

A common classification of paints distinguishes them according to the drying mechanism of the film. The more important ones are listed below.

Physical Drying Paints

The drying time is mainly determined by the evaporation rate of the solvent, which must have a great affinity with the binder. Because of this however necessary affinity, paints tend to hold the solvent back and even to absorb it from subsequent layers.
This explains why it is advisable to apply – if not specifically contra-indicated – the subsequent layers by spraying instead of using a brush or roller; in this way, the two subsequent layers do not mix through the action of the hand tools. Physical drying paints are vinyl, acrylic, chlorinated rubber and bituminous paints.

Chemical Drying Paints.

- Air-drying.
  At first solvents evaporate from the film followed by a reaction with the oxygen in the air, whose speed depends on the temperature. The lower layers of the film, which are not in contact with the oxygen, tend not to dry, because the surface layer, which dries more quickly, separates it from the air. For this reason, these products should only be applied to a low thickness. When a layer is dry enough, it becomes insoluble into the original solvents and may be recoated. Paints that belong to these classes are: alkyd and epoxy ester paints.

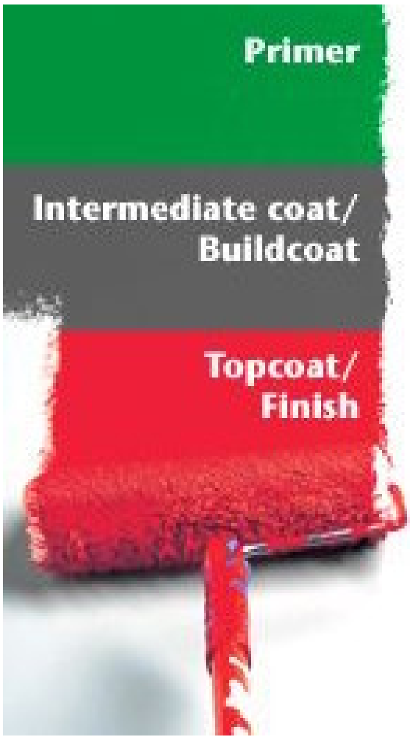
- Two-pack Paints.
  These dry with a chemical reaction of the binder together with another component (hardener). Volatile components and organic solvents evaporate after the application and guarantee a first drying, but the following and complete drying is due to a chemical reaction, whose speed is regulated by the room temperature. The components come in two separate containers, in the exact dose, and are mixed just before use. As the drying reaction starts immediately, the paint, once mixed, must be used within a limited time, called **"pot life**". Pot life changes according to the products (as it's specified on the technical sheet). However it changes with temperature.
  Once dried, the film can't be softened by the original solvents and becomes so hard it can jeopardize the adhesion of the following layers, if the times prescribed on the technical sheets are not respected.
  Two-component paints typically include: epoxy, polyurethane, polyester paints.

Combination of both.

Heat-resistant silicone paints and inorganic zinc silicates dry by solvent evaporation followed by a chemical reaction. In case of silicones, the paint is dry after the solvent's evaporation, but their best results are obtained after high-temperature polymerisation.
Zinc-silicates cure by a complex reaction of the zinc dust with the silicate binder. A certain humidity is required to facilitate the curing process but under very humid conditions without ventilation it might also extend the curing time since the water cannot evaporate from the coating.

Protection by paint systems.

Anticorrosive coating systems can be divided into 3 groups of paints according to their function in the coating system.



Primers contain inhibitive pigments that give protection against corrosion during the service life. Furthermore, they provide a good adhesion on sufficiently prepared steel and cleaned old coatings. Primers should be easily recoatable with suitable build coats or finishes.

Build coats are used as an intermediate coat in a coatings system in order to enhance the overall protection and to provide a good intercoat adhesion.
Contents of a build coat depend on the part of the ship on which it is used. In most cases they contain pigments, which reduce moisture penetration and decrease oxygen permeability. Although in some applications they are left uncoated, they are normally designed to be easily recoatable with topcoats.

As a **finishing layer**, a topcoat gives the required colour and gloss and provides protection against various influences such a sunlight, weather, abrasion and chemical attack. Besides having aesthetic purposes, finish colors also have functional purposes.
The pipes of an industrial plant are distinguished by the code-colors, according to the fluid conveyed, or the use of the fluid. Furthermore, special colors are used to make chimneys or other tall structures more visible to aircrafts.

A protective coating system should offer anticorrosive power whether by using active anticorrosive pigments such as zinc, or by using the barrier principle, aiming to prevent penetration of water or water vapour through the coating film.
It also should adhere firm to the substrate but also cohesion between paint layers must be appropriate. Also, the system must be resistant to corrosive agents and to the expected mechanical activities of the environment.

Painting steel is an efficient method of preventing corrosion. By doing so, a barrier is formed against two factors needed for initiating the corrosion process: air (containing oxygen) and moisture. However, not all coatings can be used on steel or can withstand the harsh marine environment. It is also important to realise that where a corrosion cell exists, conditions at the cathode become alkaline and therefore protective paints should resist alkali. For some applications other requirements such as acid- and chemical resistance are important too.

Paint systems are often listed according to the type of binder. Seven generic types often used in anticorrosive coatings are outlined below.

Alkyd.

Alkyd paints are one component, air-drying paints. They are saponifiable, soften in water and therefore are not suitable for constant immersion. Alkyds are easy to apply and have good levelling properties. Substrate wetting is outstanding and wire brushing as surface preparation is in most cases sufficient, which explains their popularity as maintenance paints. Although they show a good outdoor durability, alkyds are not particularly resistant to chemicals and strong solvents. Alkyd paints find their use on most areas above the waterline.

Bituminous

Bituminous paints are physically drying paints with good wetting properties. Bitumen provides the coating with a good resistance to water and moisture but has the disadvantage of bleeding into a subsequent paint coat. They are used as anticorrosive systems on underwater areas, in ballast tanks and so on.

Chlorinated rubber

Chlorinated polymer paints are one component, physically drying paints with good recoating properties. These paints are not saponifiable and therefore offer a good resistance against water and many chemicals but poor resistance against oils and solvents. A good surface preparation such as blast cleaning is preferred. Suitable for application on under and above waterline areas.

Vinyl

Vinyl paints are one component, physically drying paints and are similar in properties and use to chlorinated polymer paints. However, vinyl paints show better durability and toughness and less tendency of yellowing and chalking. Blends of vinyl polymers and coaltar (vinyltar) provide a very good resistance against water and crude oils. Vinyl tars are used on underwater areas and in ballast tanks.

Vinyl paints without tar find their use on superstructures of vessels, storage tanks and other areas subject to industrial/coastal exposure.

Epoxy

Epoxy paints are two component products and dry or cure by a chemical reaction of the epoxy resin and a hardener. The speed of this chemical reaction is by nature temperature dependent, which explains why applications of conventional epoxy paints at temperatures below 10°C are generally not recommended. However, nowadays it is possible to overcome this problem by using specially developed hardeners. Blast cleaning as surface preparation is normally required for most epoxy paints.
When properly cured, they adhere very well, show good mechanical and anticorrosive properties and offer an excellent resistance to water, chemicals, oils and many solvents.
Minimum and maximum curing times must be carefully observed when recoating epoxy paints. Epoxy paints are versatile products and can be used in principle on all vessel areas.

Polyurethane

Polyurethane paints are two component, chemically curing products. In terms of surface preparation, mechanical strength, adhesion, hardness and resistance properties, polyurethanes are comparable to epoxy paints.
However, polyurethanes are superior to epoxy paints in colour and gloss retention and chalking resistance. Therefore, polyurethane paints are often used on f.i superstructures and accommodation areas.

Zinc silicates

These products consist of two components, a binder solution and a zinc dust base. Inorganic zinc silicates cure by a chemical reaction for which a minimum relative humidity is required. Blast cleaning to minimum Sa 2½ grade is required as surface preparation. After complete curing they show an excellent resistance to corrosion, abrasion, heat and organic solvents. Inorganic zinc silicates are used on decks, in solvent tanks and also as a shop primer.

The "Properties Comparison Table" shows a review of the properties of each paints type.

	Alkyd	Bitu-minous	Chlo-rinated rubber	Vinyl	Epoxy	Ure-thane	Zinc silicate
Tolerance to lower degree of surface preparation	+ +	+ +	+	-	+	+	-
Corrosion protection	+ +	+ +	+ +	+ +	+ + +	+ +	+ + +
Gloss/colour retention	+ +	-	+	+ +	+	+ + +	-
Abrasion resistance	+	+	+	+	+ + +	+ +	+ + +
Water immersion	-	+ +	+ +	+ +	+ + +	+ +	+ + +
Acid resistance	-	-	+	+	+ +	+ +	-
Alkali resistance	-	+ +	+ +	+ +	+ + +	+ +	-
Solvent resistance	-	-	-	-	+ +	+ +	+ + +

- = Poor + = Fair + + = Good + + + = Excellent

One should bear in mind that the mentioned qualifications shown are general indications. Total paint system and surface preparation are for instance two major influences that can affect the properties and performance of paint in a positive but also in a negative way. Of course, your local Transocean Company will be more than happy to advise and assist you in selecting an appropriate paint system. However, when looking for a specific paint system, this table might help in selecting the most suitable one.