Plastic Coatings for Corrosion Scale and Paraffin Control in Oil Field Tubular Goods

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PROBLEMS OF CORROSION

Corrosion, as we speak of it, may be defined as an eating away of a material and it falls into two general categories: chemical attack, as in the action of an acid or oxygen on a metal, and electrochemical attack in which a chemical change takes place, dependent on the flow of an electrical current. This is also known as galvanic corrosion. Chemical corrosion results when a metal is placed in a reactive environment. This may be controlled by either changing the nature of the environment or insulating the metal from that environment. Usually in oil and gas corrosion we attempt the latter, either by use of inhibitors (chemical coating agents) or by the more permanent plactic coatings. In combating environmental attack, the insulating material must be completely inert to the environment and incapable of being permeated by that environment.

Electrochemical corrosion depends on the existance of dissimilarities in the metal in order to establish a current source. Commercial steel, for example, is quite capable of possessing any number of areas of dissimilar composition on one metal sample. In order for the electrochemical corrosion to take place, an electrolyte (usually impure water) must be present between the dissimilarities. A metallic conductor must also join the dissimilar areas. The metal section which aquires a positive potential is called the anode and is subject to corrosion. The cathode or negative area is protected.

To combat this type of corrosion, we can change the sign of the charge on the metal surface to be protected by installing sacrificial anodes of some more reactive metal, as in the case of galvanic corrosion control. We can also cause the metal to be protected to become the cathode by impressing a direct electric current in the right direction. A third method of preventing this type of attack is to insulate the electrolyte from the metal surface. Here again, plastic coatings can and do play an important role. The coating in this case must be completely impermeable to the electrolyte, must be a good dielectric and be able to stand all the environmental conditions present.

Plastic Coatings

Plastic coatings are by no means new. The drying oil paints, in use for hundreds of years, are a type of plastic in their dry state. We have also known of the asphaltic coatings for many hundreds of years. Of course, neither of these would be suitable for use in the severe solvent and temperature conditions encountered in modern gas and oil well corrosion. Until the beginning of the 20th century, most of the plastic coatings were natural products with slight refinements by man.

However, as the chemist began to understand some of the principals of these materials he found that he could vastly improve on nature by building his own plastic resins from synthetic chemicals. Bakeland was one of these early pioneers. He published data on the first truly synthetic plastic, the phenolic, about 1909. The following year the first production of this phenolic resin was begun. The key chemical used in this plastic was in great surplus after World War I and the utility of this plastic, plus the added availability of the raw materials, saw this industry grow by leaps and bounds.

Since the advent of the phenolic resin, a myriad of new plastics have appeared on the scene (everything from synthetic rubbers to silicones), and yet the old phenolic plastic continues to hold its own on the market as one of the leading plastics. Oddly enough, of all synthetic plastics developed to date, the first, the phenol-formaldehyde plastic, is one of the few materials meeting deeper well specifications: that is to say, a plastic that will not soften under heat and that will resist all solvents found in produced fluids and gases. In 1945 this type material became the first truly successful lining for production tubing and today it still represents the bulk of all heat reacted plastics used for oil field tubular linings. At that time all available plastic materials were tested and evaluated for this type of service.

Constant evaluation is in progress today, examining every plastic introduced to the market. To date, the thermosetting, non-oil soluable phenolic resin is still the most widely used. The properties of this material are largely dependent on the amount of linking taking place between the individual phenol groups. This material is capable of forming a very tight, three dimensional lattice structure. Of course, with one successful material on hand the search continues for other resins which might be suitable for this type application. We have found one other material which can be used in some cases - the epoxy.

Epoxy Plastics

Epoxys are rather new materials and were not commercially available until after 1950. This plastic must be reacted with some other material in order to obtain its desired properties. A number of materials can be used for this purpose: phenolic resins, urea formaldehydes, amine compounds, polyamides and fatty acids are just a few. Of this list, the phenolic resin has been proved in our laboratory testing, and confirmed by the epoxy suppliers, to be by far the best material for curing epoxy resins. The plastic formed by reacting a phenolic resin with an epoxy resin is outstandingly superior to all other epoxys in solvent resistance, acid resistance, alkali resistance, heat, abrasion and water resistance as well as hardness and adhesion.

The epoxy plastics are generally more flexible and have better caustic resistance than the straight phenolics. They are constructed like long chains joined together by phenolic groups in three or four places, while the phenolic resins are laced tightly together to form a material of low flexibility. The water and gas permeation resistance of the phenolic resin is considerably improved over the epoxy, partly due to this structural difference. The epoxy phenolic and phenolic plastics are both highly resistant to thermal, solvent and chemical attack and make acceptable materials for general oil field service. Both materials must be cured at temperatures in excess of 400° F in order to obtain maximum properties. Therefore, application is limited to those having the necessary specialized equipment.

Importance Of Coatings

A good coating is a careful balance of many factors to derive the maximum benefit from each. Coatings usually consist of three components: pigment, binder or resin, and solvent. The pigment in these highly resistant plastic finishes is not chosen for decorative purposes but rather for its ability to lend strength, elasticity, durability and chemical resistance to the film. The dry pigment is usually milled or ground into the resin component and serves to strengthen the mass, much as gravel does in concrete. The final properties of the plastic are quite dependent on the physical properties and chemical resistance of the pigment as well as the quantity of the pigment incorporated into the coating.

The resin is perhaps the most important component; it is the plastic in the plastic coating. Each manufacturer has his own research and formulation techniques and therefore the resin will vary from source to source. No two resins will be exactly alike; therefore, it is reasonable to suppose that testing is necessary to determine the best material for a given job. A coating that may be ideal in a salt water disposal line might hold up rather poorly in an oil well operating at high temperatures and pressures. The resin in its pure state is either solid or so thick that is cannot be applied by conventional methods. Therefore the third coating component - the solvent.

The solvent is usually a liquid hydrocarbon, capable of complete evaporation after the coating has been applied. It must be selected for its compatibility with the resin and its ability to evaporate in the desired time and temperature range without causing blistering or pinholing. The solvent does not form a part of the finished coating. It is the task of the coating formulator to achieve a perfect balance between the pigment, binder and resin.

Let us define a baked coating as one requiring more than 300°F for curing. Below this temperature, we are usually just force drying. A large factor in the success of a baked coating is proper curing time and temperature. This should be a very accurately determined process and adhered to very strictly by the applicator. Shortening of the time or lowering of the temperature from the designed range will result in an undercure. An undercured film will have little chemical, abrasion, or solvent resistance and will have poor cohesion and adhesion. An overcured film will become brittle and have poor resistance to deformation, chipping and impact.

Exacting Methods

Let us suppose that in testing and study we determine the best coating from a group of coatings. The battle is not yet nearly over. That coating must be applied to the surface by exacting methods. The majority of all coating failures today are due to application mistakes. The more severe the conditions encountered in service, the more exacting must be surface preparation and application. Certainly, in oil and gas field internal tubing service, these factors must be nothing short of perfect. The process varies somewhat with the applicator, but there are a number of firms applying plastic coatings of the baking types with a good degree of success today.

The basic steps that should be included in a process are cleaning, sandblasting, application and baking, with inspection at all points along the process. In the cleaning process, the tubing is first immersed in a boiling bath of hot caustic to remove any shop coatings, grease, oil and paraffin. This is followed by a rinse and an immersion in an acid tank to remove mill scale and oxides. Another rinse is necessary, followed by blasting with special equipment designed for internal sandblasting. This step produces a white metal surface which is vastly increased in total surface area. By increasing the surface area, we increase the adhesion of any coating system.

After blasting, the surface should be inspected for quality of blast and metal imperfections. Application of the coating, because of the nature of the object to be coated, requires specialized equipment. Baking is usually carried out at temperatures around 250°F in order to under cure, remove solvents and harden the individual coats. By a multiple-coat, multiple-bake system, five to seven mils of film thickness are applied to the internal portion of the tubing. When the desired thickness is obtained, the final bake is carried out at 450°F. This serves to knit the several coats together and to bring about the maximum hardness and resistant properties.

Control Of Paraffin Build Up

To this point we have generally been speaking of plastics for corrosion control. Internal plastic coatings also play an important role in the control of paraffin build up. Paraffin is a waxy material present in many producing areas. In the presence of favorable conditions, it can adhere to the sides of the tubing, restricting or completely stopping the flow.

As paraffin accumulates, pumping operations become more and more power consuming. Paraffin is in solution in the oil under higher temperatures but crystalizes out on cooling. Accumulation usually takes place where the produced fluids pass through a cooling area causing the paraffin to become insoluble. This cooling can be due to several causes: radiation, in which the heat contained in the fluid is lost to cooler surroundings, expansion of fluids through an orifice, and liberation of dissolved gases due to a reduction in pressure, to mention a few.

We seem to find some evidence that a static electric charge can be aquired by the wax particles, attracting them to the surface of the tubing. This is evidenced by the fact that plastics which usually aquire negative charges increase paraffin buildup (teflon and polystyrene), while positively charged coatings such as phenolics, in many instances, are successful in controlling paraffin deposition. It is supposed that the paraffin aquires a positive charge and is repelled by the like charged phenolic. The phenolic coating also seems to reduce the sliding friction at the tubing interface and thereby makes it more difficult for the paraffin to accumulate. Coating for paraffin has not been successful in every case, but in the majority of cases it has been found to be beneficial.

Maximum Protection

We experienced limited success in combating scale deposition caused by calcium bearing salts (calcium carbonate and sulfate). We have found teflon to be effective in this area, but due to the nature of the coating, it does not stop corrosion. In noncorrosive wells where calcium plugging takes place, teflon might well be suggested. Barium sulfate does not present much of a plugging problem because it is rare and does not normally occur in high concentrations. However, it does react with water to form mild sulfuric acid and in this case it might be advisable to protect the steel with a baking coating.

The final evaluation of an oil and gas field coating, of course, lies in the economics. Admittedly no coating is going to last forever, but the plastic coating is designed to give maximum protection to the metal for as long a time as possible. The cost of the coating for a given application must be weighed against the cost of the metal and the length of time that protection is predicted. Other factors, such as increased flow rates, paraffin control and workover costs, and down time must be considered. The cost and quality of plastic coatings continue to improve while the cost of the steel they protect continues to climb. Therefore coatings become more favorable as corrosion control agents. The economic advantage, plus continuing research and development in this plastics field, foretells an increasingly important role for plastic coatings in the future of corrosion control.