International Journal of Innovation and Applied Studies
ISSN 2028-9324 Vol. 1 No. 2 Dec. 2012, pp. 216-225

http://www.issr-journals.org/ijias/

Study an Analysis and Suggest New Mechanism of 3 Layer Polyethylene Coating Corrosion Cooling Water Pipeline in Oil Refinery in Iran

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ABSTRACT: The corrosion of pipelines' coatings is one of the main problems in oil and gas industries for which a large amount of money is spent each year. Coating is the first defense line in front of a corrosive environment in which pipes have been buried. Good function of coating depends on its adhesiveness rate to the metal surface. Initial adhesiveness and its durability in the contact conditions are among those factors that enhance coating efficiency in long term. Coverage in line pipes include of high costs. For this selecting cover and how apply is high important. Three fold polyethylene's include of epoxy layers, adhesive and polyethylene. Each other from layers having attributes that increasing its application for long term. Polyethylene layer is good shelter for prevent of physical damages. In attention to corrosion in lower temperature is an electrochemical reaction and rate of a electrochemical reaction is very impress of a element or very reactor from surface.

KEYWORDS: Polyethylene Cover, Epoxy Layer, Outer Corrosion, Initial Adhesiveness.

1 INTRODUCTION

The corrosion of pipelines' coatings is one of the main problems in oil and gas industries for which a large amount of money is spent each year. Cessation of production creates a very high loss in terms of hydrocarbon production or maintenance costs. Therefore equipment faultless during their shelf life is considered as a basic problem. Those studies which result in compilation of effective strategies, laws, protocols and methods for preventing and removing corrosion effects are studied as; corrosion management. Corrosion problem in Canada has resulted in ten times pipelines' leakage and twelve times explosions in the period of 1977 to 1996, and in our country investigating this phenomenon and its management is of extraordinary higher importance due to the fact that oil, gas and petrochemical industries have been located in corrosive environments. The reports of malfunctions due to corrosion indicates that the reason for this phenomenon is mainly due to tragic carelessness in plumbing and equipment manufacture and installation which result in explosion, fire and spread of toxic materials in living environment. besides it has some costs such as replacement of corroded equipment, shut down of plants due to replacement of corroded equipment, disturbance in processes due to equipment corrosion and impurity of processing products due to corrosion related leakage and waste of the products of those vessels which are attacked by corrosion, all of these problems make the most important costs and losses created by corrosion. The studies show that 70 percent of losses can be prevented by observing related principles and instructions. According to the report of Bartel institute one third of industries 'corrosion costs are prevented by simple applying of existing knowledge and technology. Another point which is ignored is that indirect corrosion damages are much more than direct ones. Corrosion management has the responsibility of corrosion control and installations in all respects for preserving capital and always uses advanced tools and methods in enhancing this purpose. Corrosion process is managed since the very beginning of planning installation until their servicing by corrosion management. For example a planning engineer gathers enough information from corrosion management to design structures with long and useful shelf life or amends the following work steps by using enhanced information from occurred corrosions.

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2 UNDER COATING CORROSION MECHANISMS

Under Coating Corrosion is started in presence of water and oxygen. When water and oxygen are present on the surface of a metal, corrosion occurs due to metal dissolution (anodic effect). This chemical process is balanced by oxygen reduction. Under Coating Corrosion rate depends on the kind of insulation, the amount of oxygen, the amount of impurities in the water, temperatures and the heat transfer properties of metal surface or the conditions of metal surface being wet or dry. In the absence of oxygen the amount of corrosion rate can be ignored .Although low alloy and carbon steels have the lowest corrosion rate in alkali environments but chloride ions create localized pitting under coating.

Corrosion Control Methods: Corrosion in industries is controlled by one of the following methods.

A-Corrosion-resistant alloys

B- Corrosion inhibitors

C-Stabilization method

D- Corrosion-resistant alloys

3 COATING AND THEIR ROLES IN COUNTRY'S ECONOMY AND INDUSTRY

It is quite clear that any of the coating systems have their own advantages and limitations, and that is why one of them is preferred over the other in most of the conditions. But in most other conditions both two systems can be used and it makes selection difficult. In these occasions there must be a suitable method for investigation and comparison that is a reliable guide in selecting proper system. One of the important factors in selecting proper system is cost. The importance of cost factor is such that it is dominant over other parameters and cause selection of a system based on cost. The coating of pipelines exposes a lot of items during operation such as moisture, pressure, bacteria and etc….. Applying coating over pipelines has a lot of costs, for this reason selection of coating is of much importance.

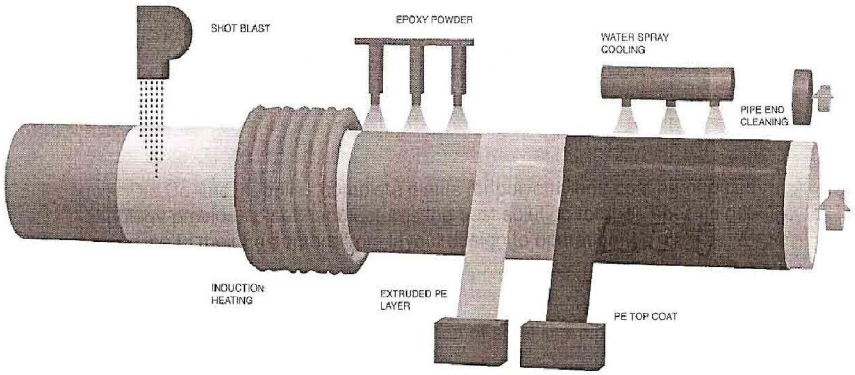


Fig. 1. View of Cover Process

Also for buried pipes underground there is the possibility that their coating must be replaced in short durations like other structures and the coating must last at least for more than 20 years. For this purpose the properties a coating needs is as follows:

1. Resistant against water and moisture: even dry soils have a little moisture and pipeline coating is often wet, for this reason coating mustn't absorb moisture because it results in weight increase and electrical resistant reduction.
2. Resistant against variable pressures: placement of pipes underground results in pipes being under pressure. Also the presence of gravel, movement of soil due to moisture and also other existing particles in the soil causes the above mentioned variable and unharmonious pressure. In fact coating must be a physical protection and not separate from surface.
3. Resistant against bacteria and mushrooms: There are a lot of bacteria in the soil which attack different materials and cause their extinction. Of course bacteria and mould attack is not so prevalent.
4. Resistant against water capillary effect: Water penetration due to capillary effect causes separation of coating from steel. Any fine crevice or gap causes the capillary effect unless the contact between coating and pipe is strong and

very sticky. In fact primer color has the duty of creating a strong adhesiveness between pipe and coating and prevents water penetration and coating separation.

5. Suitable with temperature variations: Temperature variations can be influential because the rate of steel expansion and coating is different. Expansion and shrinkage result in movement in the pipe but this movement is uniform and slow. For this reason coating must be resistant against temperature variations and not separated from the pipe.
6. Resistant against being solved: Water is capable of solving some of the materials but the coatings are insolvable in water. Also it must be investigated that coating be resistant against other solvents besides being insolvable in water especially against oil and its derivatives.
7. Resistant against absorbing soil: Soil may absorb some materials. Clay, silica gel, charcoal and some other combinations have the absorbing property. Soil always is completely in the contact with coating and absorption of some elements from coating by the soil may make coating fragile, perforated or reduce its resistance against soil.
8. Resistant against mechanical damages: besides the aforesaid items in part 2, coating must be resistant to mechanical stresses during installation or storage.

First layer: Immediately after the pipe one form of film of liquid or gum of epoxy is created, Minimum dryer thickness must be between 20-60 micron, Based on ISO 2808, epoxy powder has some materials which are used against heat that is used for three-layered poly ethylene coatings for steel pipes and must be specially formulated and designed and this is for electrical application and corrosion improvement from coating system and also providing unlimited cathode maximum resistance is suitable. Epoxy powders used in three –layered coatings is classified in two different groups. The first group has primer property and the second group has coating quality. These two materials have remarkable differences in applying, temperature and thickness; there is a tendency in industries to use epoxies with coating quality. Epoxy layer must have such an enough thickness that prevents holiday formation.

According to Dennis Neal, the manager of Harding and Neal Company of USA having experience in coatings and corrosion recommends minimum thickness of 250 micron for the epoxy layer. Time is a sensitive and critical factor in creating adhesive and poly ethylene layers. First the adhesive develops a very strong chemical bond with chemical groups in epoxy powder which is uncured therefore into this stage the epoxy must not completely cure. On the other hand adhesive and poly ethylene are connected physically which is done by rollers' pressure and time being critical and sensitive is because of epoxy for bond with adhesive must not completely cure on one hand and must get jelly condition on the other to be able to resist against rollers' pressure, in the other words all operations of these steps are done in less than a second.

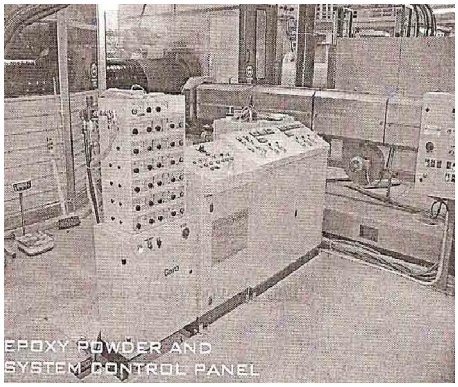


Fig. 2. View of Epoxy Controller

Coating appliers must be careful that applying a solution for three-layered coating doesn't result in another problem for example separation in the seams is reduced by lowering applying temperature of epoxy from 239.4 'C to less than 232.2'C, but although FBE is cured in lower temperature, high viscosity of molten in this temperature does not allow epoxy flow and complete wetting of metal surface on coating adhesiveness in warm condition.

Flexibility: Flexibility should be measured according to DIN 53152.

Pressure Resistance: Pressure resistance of the epoxy film should be minimum 120 kg / cm at 20 ° C was performed.

Second layer: Second layer polymer creates adhesiveness between layers 1 and 3 and must be compatible with both layers. Minimum thickness must be between 160-200 micron Thickness may increase or reduce according to the mutual agreement with customer but minimum thickness must be investigated safely.

Third layer: Polyethylene coating must be formed in this layer. Thickness must be uniform in all through the pipe and minimum general thickness must be acceptable.

Table 1. Physical Properties of Adhesive

PROPERTY	UNIT	VALUE
1) Density	g/cm^3	0.900-0.950
2) Melting index (2.16 kg/190˚C)	g/10min	0.5-8 or as suitable for application as PE (top coat)
3) Elongation	%	95 (min)
4) Melting point	˚C	9 (Typical)
5) Co monomer content	%	

Note: The test for raw epoxy power properties is under the responsibility of manufacturer.

4 ADVANTAGE BETWEEN THE SECOND AND THIRD LAYER OF COATING

Additional adhesion and chemical resistance properties are obtained by mixing epoxy. (First Layer - Corrosion Protection)

The physical and chemical force obtained by Copolymers corrosive formed (middle layer) and polyethylene (top layer)

A) Burning Process of Pipes in the Initial Stage

- Removal of surface contaminants (salts, soil, plants, oil and other contaminants)
- Minimize surface layers
- Removal the moisture

B) Methods

New air with high-pressure to remove salts and soils

Hydrocarbon solvents (family of toxic aromatic flammable hydrocarbons or minerals) to remove organic contaminants

Heating of the surface layer to remove moisture and burning the organic contaminants in dredged to clean up the temperature of 75 ° C

5 TESTS

Contractor must export the test required for all tests production covered include the company. This test should be performed 3 times over 8 hours of product. At any time in accordance with DIN 30670 standards is performed.

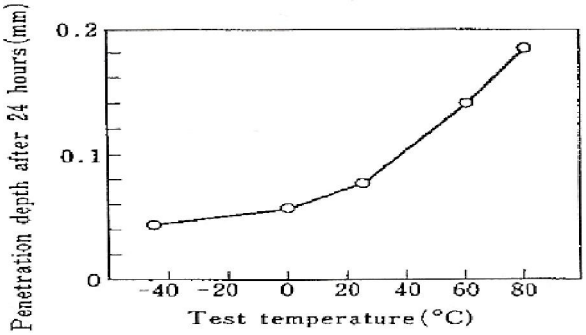
The Thickness of the Test: This test should be performed 3 times over 8 hours of product. At any time in accordance with DIN 30670 standards is performed.

Testing of Surface Tension: This test should be performed 3 times over 8 hours of product transformation, Test should be performed at room temperature and 2 purposes include of pipe lining and check of it with items on the table is desired.

Corrosion of the pipe coating layer cause to explosion of equipment so if the process do not complete for paint and coatings to be back again

Leaking water test: Leakage test (style: DIN 30670) had done in basic of heavy particle test from coverage polyethylene pipes (three fold cover). Relation between leak of water after 24 hours and temperature is shown this follow.

Chart 1. Relation between Temperature and Leakage Test after 24 Hours



Have seeing that with increasing temperature, also leakage increased.

Table 2. Physical Features of High Coating Polyethylene

Physical Properties of Top-coat Polyethylene

Physical properties	Unit	Test Method	SK ET509B (typical)
Melt Flow Rate at 190℃/2.16kg	dg/min	ASTM D1238	0.30
Density	g/cm^3	ASTM D792	0.949
Tensile Strength at yield	kg/cm^2	ASTM D638	180
Tensile Strength at Break	kg/cm^2	ASTM D638	300
Ultimate Elongation	%	ASTM D638	800
Hardness	Shore D	ASTM D2240	60
Vicat Softening Point	℃	ASTM D1525	120
Brittleness Temperature	℃	ASTM D746	< -70
Melting point	℃	ASTM D3418	128
ESCR (F50 , 10% Surfactant)	Hr	ASTM D1693	>1,000
Water Absorption	wt %	ASTM D570	< 0.01
Carbon Black Content	wt %	ASTM D1603	2.0
Oxygen Induction time at 220℃	min	ASTM D3896	15
Volume resistivity	Ω.m	ASTM D257	>10 ^{16}
Dielectric withstand	kV/mm	ASTM D149	38

The unique Rheological features of these polymers are specific that have ability of coating form in temperatures below 500 Fahrenheit.

The Relationship between Temperature and Tension: The test of tensile based on a method, has been done from simple test of polyethylene film.

Effect of Temperature : Metal surface temperature also plays an important dual role in the occurrence of corrosion under the coating. Control of corrosion under the hot coating is organizer than cold coating; the cause of this phenomenon is water vaporization under the insulation and increases the concentration of impurities with water. In closed systems, increasing the temperature, cause to accelerates the rate of electrochemical reactions and increases the corrosion rate. But in open systems, raise the temperature can increases the corrosion rate. However in open systems, raise the temperature can cause to vaporize the water, destroy the corrosive environment and reduce the corrosion rate. Also, the high temperature reduces the useful life of protective coatings. Underground pipeline of new phase wells, are with Collar coating or polyethylene strips from AL TENE that in the right performance of coverage, the problem of corrosion is not observed. Corrosion in underground pipelines is the major problems that strategic industries of oil and gas and petrochemical are facing with this. Since the pipelines in the industry play a vital role, protection and control of these structures is vital. Failures caused by corrosion in steel and other metals covered, as corrosion under coating occurs when the insulation is in proximity of moisture. Corrosion under coverage in addition to lead the costs of repair and the production is stopped; it can also jeopardize the safety of staff and facilities. Insulation and coating of pipes and tanks can be done to prevent, maintain temperature, process stability and energy efficiency. However, the dry cycles and continuous to become soggy of material under the insulation, can provide initial conditions for stress corrosion cracking or pitting corrosion.

Corrosion Mechanisms under Coating : Corrosion under coating begins in the presence of water and oxygen. When water and oxygen are present in the metal surface, corrosion occurs as a result of metal dissolution (the anode effect). This chemical process balance by reducing the oxygen, The rate of corrosion under the coating depending on the sort of insulation, the amount of available oxygen, the amount of impurities in the water, temperature and heat transfer properties of the metal surface and dry or wet conditions of metal surface. In the absence of oxygen, corrosion rate to be negligible. However, carbon steels and low alloy have typically low corrosion rate in alkaline environments, but the chloride ions (CL^-) can cause to localized pitting below of covered. If the soulphuor and nitrogen acids, which are acidic, from impurities in the water and air penetrate into the insulation, or if the water is acidic, occurs general corrosion. Sometimes, air and water impurities, especially the nitrate ion (NO_3^-) cause to outbreak of stress corrosion crack (SCC) external, under coating in carbon steels or low alloy that are not tension. Mentioned phenomenon is more significant, when the process of alternating dry and wet environment, cause to increase the concentration of impurities.

Effect of Coverage: Corrosion under insulation types is possible. Sort, only play a role in the speed and quality. The main effect of coating in this type of corrosion is to assemble annular space for gathering and remaining the water. Water can be supplied from external sources of rain or the fluids condensate.

Chemical composition and properties of coating have the role in corrosion. Covering material can absorb water and supply the proper water environment for electrochemical reactions. In addition, chemical compositions into the coating such as chloride can play a role in the electrolyte, which can accelerate corrosion.

Performed Experiments: Potantiometric experiments: To determine the properties of cathode protection Galva true, Potantiometric test adopted according to standards ASTM G 71-81, ASTM G 3-89, ASTM G 82-98, and result of this, is confirmation of properties Galva true catholic protection.

Experiments study of Mechanical Behavior: study of mechanical behavior of the coating includes measure of adhesion to the surface, test of hitting, weather tolerance, study of tolerance of thermal expansion and contraction.

Strategies for Corrosion Management: Corrosion management proceeds to offer preventative strategies in two technical and no technical domains. The topics of no technical domain as preventative strategies are as follows:

1. Enhancing the employees' awareness about the high costs of corrosion and saving costs result in correct applying of existing technologies and corrosion costs. Thus a lot of corrosion problems are due to lack of awareness about corrosion management and accountability of people in exchanging operations, inspection and maintenance of management system.
2. Changing guidelines, protocols, standards and management methods to reduce corrosion costs by correct corrosion management resulting in effective control of corrosion and safe operation and increase in shelf life of equipment.
3. Amending and generalization of employees' instruction to introduce and identifying corrosion control.

4. Changing and amending wrong belief about not being able to do anything about corrosion and making new decisions in preventing this phenomenon, also preventive strategies in technical domains are of a very high importance. Some of these strategies are as follows.
5. Upgrading planning methods and using advanced planning ones to better managing corrosion which prevents avoidable corrosion costs. In this vein planning methods must change and the best corrosion technologies must be available for planners.
6. Improving corrosion technologies via research and development. Corrosion can be controlled in most industries by using scientific methods and new technological achievements.

6 AN ANALYSIS OF REASONS FOR THREE-LAYERED POLY ETHYLENE COATING SEPARATION.

Good function of coating depends to a high extent to its adhesiveness rate to metal surface. Initial adhesiveness and its durability in contact condition are of those factors that result in high efficiency of coating in long term. The extent of initial adhesiveness has a very high relationship with coating flow and its wetting when applying coating and also with cleanliness of surface and its readiness. Durability of adhesive depends on coating properties such as its resistance against moisture penetration and also its endurance against catholic disbandment.

The most leading coatings having more consumption than other kinds are as follows:

1-FBE (fusion bonded epoxy)

2-Poly urethane (from technical view poly urethane materials are of the best coatings used since 1970 on).High cost of this coating has resulted in using it just for special cases such as when temperature is very high. Three-layered poly ethylene coating includes epoxy, adhesive and poly ethylene. Any of the layers provides coating with properties to lengthen its efficiency for a long term. Epoxy layer has a very good adhesiveness due to its transverse bonds and has a very high resistance against corrosion and oxygen penetration. But it is vulnerable to the mechanical hit when storing and line performance. Poly ethylene layer is a very good protection to prevent physical damages. A main problem with this coating is that poly ethylene does not have adhesiveness with the metal and for this reason an adhesive layer being a kind of reduced polymer is used for pasting poly ethylene to epoxy.

A) Main factors in coating separation are as follows

1. The manner three-layered poly ethylene coating (quality) of applying coating in the factory
2. Exposure Conditions and properties

Three-layered poly ethylene is one of these coatings with high efficiency, although it seems that it is used in the field in a very limited extent (comparing other coatings) and more laboratory studies and field experiences are needed to investigate if they have aforesaid properties.

7 CONCLUSION

A) Study of Cause Separation of the Coating 3-layer Polyethylene Pipeline

Pipes coating technology is developed with advanced oil and gas transmission lines. 40 years ago coal tar was the best protection for the tubes. Today, from synthesis resins used for coating and in the factory during the processes that are controlled with high precision, can be applied on the tube. The first line coating of deafens is against a corrosive environment where the pipe is buried. Second line of deafens is cathodic protection that is a vital element to keep and integrity of the lines. On the other hand, excessive protection current cause to decline of coating, to the reason for keeping the protection current in safety level, the increase efficiency of coating from the correct apply on metal surface that is fully prepared is important. Good performance of coating depends heavily on the amount adhesion to the metal surface. Initial adhesion and durability in contact situations are factors that are cause to high efficiency in the long term. The quantity of initial adhesion has the relationship with flow of coating and wetting of the surface by applying a coating and depends on clean and ready of the pipe surface.

Polyurethane (from a technical point of view and the polyurethane substance is the best type of coating that used from1970 and standards of the Draft recommended, DIN 30677-1998, DIN-30617-1992, ANSI/AWWA-C222-99 practice NACE-TG281-2002 is written for this coating. The high cost of this coverage is that, it is mainly used in special cases, such as locations with high heat.

Three-layer polyethylene coating is containing epoxy layers, adhesive and polyethylene. Each layer provides properties for cover to increased performance for long life. Epoxy layer, which provides cross-links have very good adhesion, and show high resistance against corrosion and the oxygen penetration, but against the mechanical impacts at the time of stored, is vulnerable run and transport of the line. Layer of polyethylene is a very good protective to prevent physical damage. The major problem that is with this coverage, there is no adhesion between polyethylene and metal, so that used to adhesive layer that is a polymer modified for bonding of epoxy to the polyethylene.

B) Compared to Existing Standards and Specifications for the 3 Layer Polyethylene Coating

3 layer polyethylene coating are described on the distinct national standards. The oldest and most common of those is the German standard DIN 30670 (two layers) , French standard NF A49-710 which is used in smaller scale and the Canadian standard CSA Z7245.21 which first appeared in the early 90 and in the past few years gradually find international confirmation . These standards not only are different in the specification, how to process control and testing procedure, but they have their own philosophy. The major weakness in the DIN standard is that provider of coverage don't required to use of primer (epoxy), also are not called for cathode disbandment test, and clear value to peal adhesion is very low. French standard NF has identified many weaknesses.

Canadian CSA Standard for polyethylene provides thickness of 2 to 3 times narrower than the DIN, because it is denser than of polyethylene that is used in Canada.

C) Major Factors in Coating Disband in Tubes Coated with Polyethylene

The separation depends on the following factors:

1. How (quality) factory applied coating
2. The conditions and characteristics of coating exposure, the epoxy powders that are used in three layers of coatings, classified in two different groups. First group that has the property of the primer and second group that has coating quality, these materials have significant differences in terms of apply and thickness and temperature, and generally in the industries is tend to use of high quality epoxy coating. Because the final consumer can be determine higher thickness that will result better properties for system. Study of reference list of company Jotun Powder Coating, UK demonstrates the use of epoxy layer with thickness higher of 150 microns, especially is in pipes at higher size. Epoxy layer must have sufficient thickness so should be avoided as to create holiday. Early experiences and experiments that having done in the field show increase more than 40 holidays of 40 feet for a layer with thickness of 150 microns. According to Dennis Neal advice, President Company U.S.A Harding & Neal that has a long history in the field of coatings and corrosion should be considered a minimum thickness of 250 micron for epoxy layer. Time is important and sensitive factor in the run- layers of adhesive and polyethylene on epoxy. At first adhesive with the chemical groups in the epoxy powder that are still uncured to establish a strong chemical bond, so at this stage epoxy should not be fully trained. On the other hand the adhesive and polyethylene connected physically. This is done by pressure through rollers and being sensitive of time is for this reason that from one side epoxy for bonding with adhesive should not be thoroughly cooked and the other hand should be get gel-like state, so can resistance against pressure of rollers, on other words, all of these steps must be performed in less than a few seconds. Users of coating should be careful that applying a solution for resolve the issues three layers do not cause another problem. For example, the separation at the seams with lower the temperature epoxy decreases of 239/ 4 degrees C to less than 2 / 232 ° C3i, but while the FBE at lower temperatures to be cultivated, but the high viscosity of the melt in the heat doesn't allow to flow epoxy and complete wetting of the metal surface, and this cause will be to opposite effect in terms of heat and moisture on the adhesion of coatings and too catholic voltage. Below context is from Dennis Neal, one of the exporters in coating.

Disbandment occurs on 3layer coating at STEEL/FBE interface. The extent of disbandment depends on exposure conditions and quality of the coating.

Two problems are quite widespread:

i) The FBE layer is under cured because the application temperature is low to allow the adhesive to chemically bond to FBE.

ii) There is no adhesion between the FBE and the adhesive because the temperature is higher and the FBE is fully cured before the adhesive is applied. In article from one of the company's CEPA (Canadian Energy Pipeline Association) result of experience in this company is expressed to prevention of a SCC by system covered. In this article mentioned: the best proven method for reducing SCC in a new pipeline, is use of high-efficiency coatings and effective catholic protection. Coatings must necessarily possess the following characteristics.

3. Pipe surface must be separate from contact with the electrolyte or environment that causes. (Covered with a metal surface has durable adhesion)
4. The separation of the coating, the cathode protection can with cross of coating carrying to metal surface
5. During the preparation of surface for coating, pipe so the change that is less susceptible to SCC
6. 3 layers polyethylene is one of the coatings with high efficiency. Although it appears that the limited (compared to other coatings) has been used in fields
7. Study of Reference list of the companies such as Socothern (Italy) and Corinth pipe work (Greece) and Jotun powder coating (UK), which is include pipe diameter, type of coverage and other data, indicate that mainly pipes are covered under 24 inches 3 layer polyethylene coating. In panel that recently was formed by experts of corrosion in Britain and America, and resulting is published in an article titled US & UK Industry discusses key challenges: in the Journal of Pipeline & gas journal monthly. John T Oshea former chairman of the British Institute of corrosion, after pose of status of gas network in Britain and its coverage in the high pressure line (164000 km) says: These lines are constantly developed for responsibility to the increased demand and new lines of high diameter are protected against corrosion by use of coatings with high integrity coating. Oshea in answer to the question of what kind of high integrity coating is this coating? Says: Examples of these are fusion bonded epoxy and multi component liquid coating (polyurethane) and don't pointing to use of coating 3 layers polyethylene for coating of pipe diameter.

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