A RECENT BREAKTHROUGH IN SHRINK FILM TECHNOLOGY

Boris Miksic

Barry Rudman Cortec Corporation 4119 White Bear Parkway St. Paul, MN 55110 U.S.A. (612)-429-110 Fax (612) 429-1122

1 ABSTRACT

A new shrink film has been developed that provides complete protection to components with sensitive surfaces. This new patented material provides corrosion protection and protection from abrasion and other problems associated with conventional shrink films.

Corrosion protection is achieved in two ways. Firstly, the film contains VCIs (Volatile Corrosion Inhibitors). The VCI volatilizes within the package, condenses on the metal surface and it passivates the metal surface. A second means of corrosion protection is offered by the anti condensing nature of the inner layer of this new shrink film. This inner layer wicks water away from the surface, thus reducing corrosion.

The inner layer of this shrink film also provides protection from mechanical damage. The inner layer provides cushioning to prevent damage due to impact. Additionally, the inner layer is also non-abrasive, preventing damage caused by shuffling of the film against the surface. The film is so non abrasive that it does not damage freshly or uncured coatings.

It is the revolutionary structure of this material that gives it these unique properties.

The outer layer is a special shrink film that contains copolymers. The middle layer is a hot melt adhesive that is used to laminate a nonwoven to the shrink film. The inner layer is a nonwoven that provides cushioning and abrasion resistance.

2 INTRODUCTION

The corrosion of metals during storage and shipment has long been a problem in numerous industries. Over three hundred billion dollars was spent last year alone replacing corroded steel in the United States.

3 Background

Numerous methods have been developed to combat corrosion. One such methods is the use of shrink films. These films are designed in a manner that causes them to shrink when heat is applied to them. By shrinking the film is supposed to conform to its contents. Through this conformity it is desired that the film will serve as a barrier material and prevent corrosion. There are many drawbacks to the use of conventional shrink films, not the least of which is corrosion. This paper discusses a recent breakthrough in shrink films that eliminates the problems associated with conventional shrink films.

3.1 Standard shrink films

Conventional shrink films are known to have several disadvantages. Firstly, they can abrade the protected item causing damage to the surface of the item. Secondly, these films become brittle at lower temperatures. Additionally, higher temperatures cause these films to soften and adhere to the substrate. This also causes surface damage. These films also allow a great deal of condensation on the surface, resulting in corrosion and damage to metal surfaces. Finally, these films do little to prevent corrosion of the contents. Therefore, improving conventional shrink films would result in significant advantages.

3.2 The new shrink film

This new film is multifunctional by design. One of the objectives was to design a shrink film that would prevent marring of uncured paint systems. Another requirement was that this film would be used outside with little or no shelter. Finally, it was desired to develop a product that provided active corrosion protection through the use of volatile corrosion inhibitors (VCIs). In short, it was desired to eliminate many of the problems that plague conventional shrink films.

3.2.1 Construction

It was readily apparent that the standard constructions would not meet the design criteria. A completely new construction would need to be developed. The new construction would need to have several features and therefore would require several components.

The new construction that was developed is a three layer composite. Each layer is made of a different material that provides different characteristics. The three layers are laminated together to produce a composite that contains the desired properties. By using a composite material it was possible to take advantage of the desirable properties of each component material.

Examination and discussion of each layer will facilitate a greater understanding of this new construction. Each layer provides different properties that when combined result in a film that provides total protection to its contents.

The outside layer is a specially designed shrink film. The film contains ethylene vinyl acetate (EVA) copolymers. The addition of EVA prevents low temperature embrittlement. The EVA also prevents softening at higher temperatures. The result is a shrink film that has a greater flexibility at extremes in temperature. This layer also allows the film to conform to its contents. Thus the addition of EVA to a shrink film results in a shrink film that has excellent physical properties at extremes in temperature.

The middle layer serves several purposes as well. The material that is used to make the middle layer is a VCI hot melt adhesive. The adhesive is used to hold the outside and inside layers together. Additionally, the adhesive is applied in a manner that it actually reinforces the construction, giving it better physical properties. Finally, the adhesive that is used contains a VCI. The addition of the VCI gives the material active corrosion protection.

The VCI that was chosen is also multifunctional. The VCI that was added contains inhibitors for multimetals. The VCI will provide protection to steel, copper, aluminum, and many alloys. By using a multimetal VCI the film provides corrosion protection to most engineering metals.

The inside layer also provides some unique properties as well. The inside layer is made from a spun nonwoven fabric. This nonwoven layer is inert, preventing it from reacting with the surface of the metal. Also, this layer is hydrophilic, thus it wicks water away from the metallic surface. This is a secondary means of corrosion control. In addition, this layer is very soft,

preventing surface damage due to abrasion. The use of this unique nonwoven material results in an inner layer that reduces condensation, eliminates abrasion and protects delicate surfaces.

3.2.2 Effects of the shrinking process

While the construction of this new shrink film results in its multifunctionality, the shrinking process is an integral part of this composites performance. The finished product is not made until the film has been shrunk. Each layer responds differently to the shrinking process.

The outside layer is designed to shrink and conform to the contents. The application of heat to the outside layer causes it to shrink. It is more thermally stable than conventional shrink films and therefore overheating it is less likely to damage it.

While the outer layer is shrinking the middle layer is simply heated. The heating of the middle has two effects.

The first effect that heating has is to soften the adhesive. This is important as it allows some areas of the nonwoven to delaminate and others to remain bonded to the outside layer. This softening is a critical portion of the inner layer providing cushioning.

The other effect that heating of the middle layer has is to increase the vapor pressure of the VCI. This is important as the air enclosed within the film will very rapidly become saturated with VCIs. This occurs much faster than with standard VCI films. This is beneficial because it is in the early stages of packaging that materials are the most vulnerable to corrosion. By increasing the temperature of the middle layer the VCIs are forced to migrate much faster, providing corrosion protection much sooner.

Up to ninety percent of the heat that is applied is absorbed by the first two layers. This means that the temperature of the contents only rises slightly while the exterior is exposed to much higher temperatures. The result is that the contents are much less likely to be damaged by heat.

The result of heating the shrink film is dramatic on the inside layer. Since this layer does not shrink its surface area remains the same. The external surface area however has decreased since the film has shrunk. This causes the inside layer to buckle. It uses a greater volume to distribute across its unchanged surface area. This gives rise to its cushioning properties as illustrated in figure I.

3.2.3 Surface protection

Protection of the surface of the contents is critical to preserving its value. The contents may be ruined if they arrive scratched and badly damaged. Also, the contents may be just as readily ruined by corrosion. Therefore it is important to provide total protection.

The soft inside layer prevents numerous types of damage from occurring. Firstly, due to its non-abrasive nature shuffling of the film will not scratch the surface. This material has been found to be safe for uncured painted surfaces. Additionally, this layer is inert and therefore will not react with the surface or induce corrosion. Finally, the anti-condensing nature of this material eliminates damage caused by water.

Protecting the surface from physical damage is important. Equally important is to protect the surface from chemical damage caused by corrosion.

3.2.4 Corrosion protection

This new material has several features which combine to provide excellent corrosion protection. These features individually are effective at controlling corrosion. When combined they have a synergistic effect and dramatically increase the corrosion protection offered.

There are two types of corrosion protection offered by this material. Firstly, it contains VCIs which provide proactive corrosion control. Secondly due to the hydrophilic nature of the inside layer, the material also provides reactive corrosion control.

The principles of VCIs are rather unique. VCIs function similar to conventional corrosion inhibitors in contact. However, the difference is that the inhibitor is volatile. First the inhibitor volatilizes from the hot melt adhesive. Next it diffuses through the porous nonwoven fabric and vaporizes inside the package. The VCIs condense on the metal surface forming physically adsorbed layer. This monomolecular layer protects the metal from corrosion.

The volatility of the inhibitor gives it some unique advantages. Because the inhibitor is volatile it diffuses through the air to the metal surface. The component to be protected does not need to be in direct contact with the film surface. Additionally, the VCIs are virtually undetectable on the surface of the metal and thus do not interfere with the properties of the metal or non-metallic such as glass rubber or plastics. Finally, the VCIs do not need to be removed prior to further processing of the metal or equipment being put into service.

The VCIs in this film prevent corrosion due to a variety of conditions. There are many contaminants that can accelerate corrosion. Chlorides, sulphur dioxide and heavy condensation often lead to rapid corrosion. These VCIs have shown the ability to protect metals even in these harsh environments.

4 CORROSION TESTING

In order to determine the ability of this new material to prevent corrosion it was desired to test it in a variety of conditions. Three tests were chosen to evaluate the performance of this new material. In each test the performance of the new shrink film was tested against a control sample. The control sample was made using the same construction, except that no VCI was added to the adhesive layer.

The first two tests that were used were developed by the Cortec Corporation research and development team. The third test is based upon previously published works.

4.1 SO2 Test

The first test that was used is called the SO_2 test. For this test method SO_2 is used to accelerate corrosion in a controlled atmosphere.

SAE carbon steel 1010 panels were washed with methanol and allowed to dry. Pouches made of the new shrink film were made. The panels were placed inside the pouches and heat sealed. This was repeated using a control sample that contained no VCI. The pouches were placed inside the one gallon jar. A small beaker containing 0.04 g of sodium thiosulfate was placed inside the jar. A 50 ml beaker containing 30 ml of an aqueous solution containing 1% ammonium chloride and 1% sodium sulfate was also placed inside the jar. Finally, 0.5 ml of 1N sulfuric acid was added directly to the sodium thiosulfate. The jar was quickly capped. The jar was then heated to 50°C for sixteen hours. Then the jar was at ambient temperature for eight hours. The panels were removed from the jars, unwrapped and inspected for signs of corrosion.

4.2 F-12 Test

The second test that was used has been named the F-12 test. The conditions that are used to accelerate corrosion in this test are cycling temperatures that cause condensation. This attempts to reproduce and accelerate the conditions that occur in warehouses and other facilities without climate control.

The panels were cleaned and wrapped in pouches in the same manner as they were for the SO_2 test. The panels were then placed in one quart glass jars. A 50 ml beaker containing 30 ml of an aqueous solution consisting of 1% ammonium chloride and 1% sodium sulfate was also placed inside the jars. The jars were then sealed and placed in an oven programmed to cycle for sixteen hours at 50°C and eight hours at the ambient temperature. This cycle was repeated eight times. After the eighth cycle the panels were removed from the jars, unwrapped and inspected for signs of corrosion.

4.3 Prohesion Test

The third test that was used is called the prohesion test. The prohesion test also is cyclical. There is a dry cycle with an elevated temperature and a wet cycle in which an aqueous solution is misted into the chamber.

For the third test it was desired to use an actual real world part. Two types of gun barrels were used, stainless steel and carbon steel. The barrels were cleaned, allowed to dry and placed in bags made from the new shrink film. As before a control sample was also used. The bags were then placed in the prohesion chamber for two weeks.

The prohesion test is similar to the salt spray test, ASTM-B117, with a few modifications. The prohesion test uses a spray at ambient temperatures of an aqueous solution of 0.4 % ammonium sulphate and 0.5% sodium chloride. This portion lasts one hour. The next step is dry (no spray) with the temperature elevated to 35°C. This lasts one hour also. One complete cycle is two hours long.

5 RESULTS

6 CONCLUSIONS

This new shrink film offers tremendous advantages over conventional shrink films. This new material provides total protection to its contents.

The results show that this material offers protection to components in a wide variety of corrosive conditions. Based upon the SO_2 test results this new shrink film provides corrosion protection even in conditions of heavy industrial type contamination. Furthermore, the F-12 test show that under conditions of cycling temperatures and heavy condensation this film is able to protect its contents from corrosion. Finally, the prohesion test shows that this material is effective in controlling corrosion of "real world" parts even in an atmosphere laden with chlorides.

To conclude, this new material is a vast improvement over conventional shrink films in that it is able to protect its contents from physical damage as well as damage caused by corrosion and therefore provides complete protection.