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New Technology for Vapor Corrosion Inhibiting (VCI) Transparent Plastic Packaging Combined with Acid-gas Scavenging (AGS)

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ABSTRACT

Acid-gas scavenging films (AGS) have existed in two forms, both with fillers that chemically react to reduce diffusion of acid-gases into sealed bags. These provide corrosion protection from acid-gases exterior to the package. They have no effect on corrosion in the presence of humidity and oxygen inside the enclosure. One form, called AGS-Cu in this paper, is opaque and contains copper and carbon particles. The other, called AGS, uses transparent inorganic oxide fillers, primarily to mitigate tarnishing of silver and silverware. A new technology combines AGS and Vapor Corrosion Inhibitor additives (VCI and VPI) for superior corrosion protection of multiple metals from the effects of internal humidity and external acid-gases. Test data show that combined VCI & AGS give best corrosion protection for a wider range of metals and atmospheric contaminants than VCI and AGS alone. Corrosion testing should consider the confounding effects of VCI, AGS and desiccation.

Keywords: atmosphere, acid-gas, corrosion, tarnish, inhibitor, scavenger, volatile, vapor, AGS, VCI, VPI, ferrous, non-ferrous, copper, silver

INTRODUCTION

Protection of metal components from atmospheric corrosion remains a pervasive and costly problem during storage and shipment, particularly when packaged parts and equipment must remain clean of coatings and contaminants after removal from the package or container. Packaging materials containing vapor corrosion inhibitors (VCI or VPI or VPCI) are known to provide cost effective and proven corrosion protection in many applications, but there are also variations in performance among manufacturers and formulations that reflect the relative rates of the specific inhibitor system in comparison with aggressive contaminants other than warm-humidity, such as acidic surface residues from fingerprints or even from effects of anaerobic bacterial activity in poorly maintained metal forming wash and cutting solutions. Certain atmospheric contaminants, such as strong acid gas pollutants, may also diffuse through sealed VCI packaging to compete in rate with the inhibitor protection. In general these effects are mitigated by use of good practices in the manufacturing and packaging of metal parts, but these effects are also a consideration in the ongoing evolution of robust and general purpose VCI products.

A fundamental invention[1] first taught how to incorporate VCI formulations into melted polyolefin plastics, particularly polyethylene (PE), for processing into packaging film and bag materials. Other related plastic forms and VCI formulations followed, and the technology continues to evolve to serve a still widening range of applications. The effectiveness and cost advantages of VCI packaging for protecting parts and systems from corrosion has resulted in their replacing oil coatings and desiccants in many commercial and military applications, as illustrated in several case studies of ocean transshipments of automotive and electronics components[2] as also illustrated in figures 1 and 2.

The addition of VCI properties to PE packaging films and bags makes them capable of largely overcoming the effects of water vapor in combination with most contaminants on the metal parts to be protected. However, diffusion into a sealed package may become a consideration when the external atmosphere has an exceptionally high level of acid gas contamination. A first consideration is that the rate of acceleration of corrosion from the acid-gas contaminants that diffuse through the package may exceed by several orders of magnitude the rate of corrosion by the presence of moisture alone. A second consideration is that some VCI systems may have their useful life reduced by reaction of the acid-gas with the VCI additive in the packaging material. It is in these exceptional conditions that recently patented transparent plastic film materials provide a chemical barrier effect to acid-gases by the addition of small concentrations of metal oxides into the plastic. The effect of these additives is called Acid-gas Scavenging (AGS) or AGS Tarnish Inhibitors (AGS-TI) in this paper.[3] Another recent patent relates to the synergistic combination of VCI and these AGS-TI additives.[4] Otherwise, the properties of these synergistic films is similar to what is expected of VCI films in general. Their transparency permits inspection parts and labels, and the AGS effects have comparable shelf life and service life to VCI materials. Methods of testing and test results are provide in relation to materials that make similar claims without comparable performance.

Plastic films are used as physical barriers to protect items, but even tightly sealed bags, such as PE film of thicknesses in the range of 25 to 200 microns (1 to 8 mils), are semi-permeable to water vapor, acid and other gas contaminants that may diffuse through them at rates that vary with the thickness and material type. For example, typical PE film has a typical water vapor transmission rate (WVTR)[5] of about 1-2 grams of water per 100inch^2 per day for standard 1 mil thickness under standard conditions of relative humidity 90% difference between opposite sides of the film and temperature of 100^{o}F.

In contrast, special multilayer composite barrier materials are available that exhibit at least two or more orders of magnitude lower transmission rates for water vapor and other gases than for PE films. An example is layered composite films that include metal foil or certain vacuum metalized plastic substrates. Such materials are required for food packaging as well as applications where a desiccant must be used to remove moisture from the interior of packages without being overwhelmed by continuous diffusion of moisture through even a perfectly sealed package. AGS barrier additives to plastic packaging films should perform comparably with these special physical barriers to acid-gas diffusion. This rate also decreases roughly in proportion to increased film thickness and to the RH% differential, and is strongly dependent on the temperature.

For decades there have been non-VCI cloth, plastic and composite bag and wrapping materials that claim to protect silverware, coins or electronic components from tarnish with claims that the bag has a barrier effect, either physical or chemical, therefore with AGS effects. Such non-VCI materials are generally opaque or darkly colored if there is sufficient AGS additive to have a measurable effect. For example, cloth materials impregnated with activated carbon have been widely available for decades, but there is no barrier to moisture and there remains some degree of diffusion to acid gas by the nature of the partial physical barrier of the fabric. Claims for AGS properties in these and other materials, such as plastic films containing copper and carbon, are not always substantiated with comparitive test data that permits one to judge how much the claimed effect is mostly that of a physical barrier.

A class of film materials, called AGS-Cu in this paper, described in a 1990 patent[6], were initially created for packaging of electronics components, for which electrostatic charge dissipation (ESD) is also a requirement. These AGS-Cu films generally contain substantial concentrations of fine copper particles, sometimes also containing fine carbon particles. They are correspondingly opaque, having a color that is either like that of copper or of carbon-black. Claims are made that they also protection metals from corrosion, both in the presence of acid-gas contaminants that may diffuse from outside to inside the package as well as extraordinary claims that they provide more general corrosion protection for multiple metals in the presence of water vapor and other contaminants inside the package that is supposedly comparable to the best VCI materials. Within the past decade or more, as commodity prices like copper reached record levels, there were also cheaper derivatives of this basic technology that evidently had substantially reduced concentrations of copper from what is described in the patent. These materials offer correspondingly reduced AGS effects, if any, and may be semi-transparent with only a copper tint. In general, marketing claims for these AGS-Cu products may not live up to the claims, especially for corrosion protection in humid environments, whether for ferrous or non-ferrous metals. A recent paper reported analysis and evaluation of some of these materials for their relative corrosion protection for carbon steel in humid environments.[7] The paper concluded with the following summary.

> "In humid air climates, it is found that the copper and carbon particles dispersed in PE films cannot protect mild steel against corrosion. There is no difference in the protective behavior between PE films with and without these particles. On the basis of EIS data it can be concluded that the dispersed copper is electrochemically inactive … It could be noticed that the corrosion of mild steel depends on the relative humidity inside the package and cannot be inhibited by the copper particles dispersed in the PE Film. In humid air conditions, a better protection performance can be achieved with films containing contact or volatile corrosion inhibitors …"

Some additional findings about these films for the relative corrosion protection of these AGS-Cu films for non-ferrous metals in the presence of acid-gas environments was included in tests summarized below.

A new form of AGS packaging film, called AGS-TI and mentioned earlier in this introduction, is considered both for its tarnishing inhibiting (TI) properties alone as well as for synergistic properties in combination with some VCI additives. Tests summarized in this paper are a basis for claims on behalf of the new materials, including some comparisons of performance compared with representative AGS-Cu materials like those that were also analyzed and tested for rust prevention with ferrous metals in the quoted summary above.

EXPERIMENTAL METHODS

The most common conditions for testing packaging films are simply to use warm humidity, whether with steady-state[8, 9] or the cyclic conditions[10]. These conditions generally achieve relatively quick results with steel specimens – typically in days to months depending on the corrosion protective properties of the packaging film. When non-ferrous metal specimens are used, these conditions generally do not provide sufficient acceleration to achieve results even in months. Therefore, it is common practice to enhance corrosion rates by the addition of "salt fog" to simulate proximity to ocean conditions other chloride-rich environments[11] or to add acid gas components, as is done here. The specific choice of test conditions varies with the manufacturer or user depending on actual packaging applications to which the accelerated test is expected to relate. It is also useful for rapid evaluation of new materials, whether for product development or for routine quality evaluations, to use relatively simple apparatus, such as a "jar" rather than using standardized lab test chambers.

An example of a "jar" test, using only temperature and humidity as accelerants with ferrous metal specimens, is for Vapor Inhibiting Ability (VIA-F).[12] This standard method is used to evaluate certain performance aspects of VCI materials. Considerations for similar testing for non-ferrous metal specimens is considered in a related paper in this symposium[13]

Two non-standard "jar" methods were used in the current study to quickly assess packaging materials in the presence of extreme acid-gas conditions. Acid-gas concentrations may reach as much as 2000 ppm (0.2%) when the "jar" apparatus is warmed to 50°C (122°F). In general these conditions achieve several orders of magnitude greater acid-gas concentrations than the most unfavorable city and industrial environments. Two more acid gases may be combined in the same jar to produce even more intense effects. This is done by simply adding separate beakers of the reagents outlined below. Test details may differ among specific tests to achieve alternative degrees of acceleration, such as using ambient lab temperature or elevated temperature (by placing jars in oven conditions, typically at 50°C (120°F), or by cycling between these ambient and oven conditions after periods of 4 to 24 hours. Cycles may be repeated if necessary, but the acceleration is generally sufficient to show significant relative performance between the film material used in test samples and the failure of a "control" made from plain polyethylene (PE) film of the same thickness of the test sample, the latter containing additives for corrosion protective properties, such as the VCI and AGS.

Sample preparation

Carbon-steel 1010 samples were either polished with fine-grit 400 abrasive, or panels 2" x 3" in size with pre-polished surfaces were used. Non-ferrous samples (copper and silver) were prepared by using a tarnish remover and subsequently rinsed with deionized water. All samples were kept clean and dry at very low RH% until being sealed bags of the plastic film sample material. Each cleaned and bagged metal specimen was suspended in a separate jar apparatus without being allowed to touch the reagent solutions in the bottom of each jar.

Inspection Criteria

Each test was concluded when the "control" specimen, sealed in an untreated PE bag, showed discoloration (tarnish or other surface changes). A relative "pass" for metal samples in treated packaging must show NO visible tarnish or discoloration after the selected exposure time. Specimens that display relative "failure" have visible surface alteration, tarnishing or discoloration.

Ratings for steel panels are generally described in approximate percentages of "rust spots". More uniform changes in color or darkening for copper or silver are judged after mild washing with alcohol and water to distinguish light stains from "corrosion"

Jar Test with high concentration of hydrogen sulfide

Hydrogen sulfide is introduced into some test jars by placing a 1% solution of ammonium sulfide in a small beaker at the bottom of the test jar that is then sealed after a metal specimen in a sealed sample bag is hung from the top of the jar. The reaction in humid air may be characterized as follows.

$$(NH_4)_2S \rightarrow H_2S + 2(NH_3)$$

A related test method is mentioned in a previous NACE paper[14] in which the concentrated H_2S is created in the presence of warm wet humidity by the reaction with ferrous sulfide (FeS) and hydrochloric acid (HCl).

Jar Test with high concentration of sulfur dioxide

A small beaker of dilute sodium thiosulphate (also called sodium hyposulfite, $Na_2S_2O_3$) is placed into a jar that also contains a small amount of water in the bottom. A metal specimen in a sealed sample bag is hung from the top of the jar. Dilute sulfuric acid is added to this jar at the moment it is sealed, releasing sulfur dioxide with byproducts of sodium sulfate and precipitated sulfur. With opaque packaging the bags were opened and resealed for each 24 hour cycle, whether the apparatus was subjected only to room temperature or cycled between room temperature and oven temperature.

A similar test method is mentioned in a patents[3, 4] and a NACE paper[14]. They also mention an optional second small beaker to maintain about 95 %RH by the combination of 1% solutions of sodium sulfate and ammonium chloride.

Chamber with sulfur dioxide

Chamber conditions that are not part of any standard test method were also used for some tests in which relatively high concentrations of sulfur dioxide were injected into an environment that was maintained at 38°C (100°F with saturating relative humidity (95-100%). Sulfur dioxide gas was injected for 15 seconds each cycle of 60 minutes with a flow rate of 460 cm^3/min. Each injection provided about one mole concentration of sulfur dioxide per liter of chamber volume (approximately 5×10^{-6}). Average non-equilibrium concentration is estimated to be in the magnitude of 50-200 ppm from the balance among consumption for corrosion, dissolution in water, air circulation and exhaust.

Metal specimens

The following metal specimens were used. Test results are essentially identical with copper water-pipe elbows and cold rolled panels.

- Steel panels. Type 1010 to 1018 cold rolled carbon-steel
- Copper panels, cold rolled
- Copper elbows, water-pipe component
- Silver spoons
- Silver winding over steel. guitar strings
- Zinc plated mild steel, fine grain layer, thickness about 18 µm
- Phosphor-bronze winding over steel, guitar strings

Packaging film samples

Selected materials represent two categories of AGS in addition to plain PE (no additives).
Bags 3.5 – 4 mils wall thickness

- Polyethylene (PE)
- PE with VCI
- PE with AGS-Cu, opaque with copper powder filler
- PE with AGS-TI, transparent with metal oxide filler
- PE with combined AGS-TI and VCI

RESULTS

Jar Tests with high concentrations of sulfur dioxide

Paired tests were conducted for various forms of silver, copper, phosphor bronze and steel specimens for relative performance in “control” bags of plain PE compared with bags containing AGS-TI, both with and without augmentation with VCI. Each paired tests was terminated within a day when metal specimens in PE were heavily corroded. All combinations of metal specimens in AGS-TI with and without VCI showed no visible corrosion with the exception that the combination of AGS-TI with

VCI gave slightly longer protection for steel specimens than VCI alone. Specimens of AGS-Cu had moderate corrosion of metal specimens when there was no corrosion in comparable AGS-TI bags.

Jar Tests with high concentrations of hydrogen sulfide

Paired tests were conducted for various forms of silver, copper and steel for relative performance in “control” bags of plain PE compared with bags containing AGS-TI. Each paired tests was terminated within a day when metal specimens in PE were heavily corroded. Silver and copper specimens in showed no visible corrosion. There was no result for specimens of steel since there was not sufficient effect from hydrogen sulfide to corrode either the specimens in PE or in the AGS-TI.

Chamber tests with sulfur dioxide

Paired tests were conducted with copper and steel specimens for relative performance in “control” bags of plain PE compared with bags containing AGS-TI. Control specimens in PE bags failed within 3 days, with steel specimens having 10 to 100% rusted surface area and copper being darkened (red-black). In comparison, specimens of both metals in AGS-Cu failed within 3 to 7 days. Specimens of both metals in VCI bags had no corrosion when tests were terminated after 20 days or more.

CONCLUSIONS

Some VCI packaging films may have limitations in performance in the presence of high concentrations of environmental acid-gases. Transparent packaging films containing metal oxide powders, as described in recent patents, demonstrate corrosion inhibition for metals against high concentrations of external atmospheric acid gases. These tarnishing-inhibiting (AGS-TI) additives may be used alone for applications of extreme sensitivity or general concern about possible interactions of vapor inhibitor components with objects being protected, such as special applications in the electronics industry. When also used in combination with VCI additives, the new AGS-TI additives provide synergistic benefits to protect multiple metals under extreme acid gas conditions.

In general, these VCI and AGS-TI additives give better corrosion protection for a wider range of metals and atmospheric contaminants than films with additives for either VCI or AGS alone. Corrosion testing should consider the confounding effects of VCI and AGS as well as of possible desiccation.

Other types packaging films that claim to provide corrosion protection by means of fine copper particles embedded in the plastic materials, sometimes augmented with carbon, did not measure up to claims of a 1990 patent and related sales promotions of currently available versions of these materials.

ACKNOWLEDGEMENTS

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Figure 1 - Clean, oil-free crankshafts, each in a closed VCI bag in layered pallet for ocean shipment to assembly plant.

Figure 2 – Engines in sealed VCI bags during long-term storage and subsequent ocean shipment.