

HP 152a

Aerosol Propellant

Corrosion Inhibitors for Water-Based HP 152a Aerosol Formulations by J. A. Creazzo Wilmington, DE

Technical Information

Introduction

Reformulation of any aerosol product has many challenges. In an attempt to meet regulations limiting the volatile organic compound (VOC) content of consumer products, many formulators are developing products with higher levels of water.

Water-based formulations have many advantages, including, in many cases, lower cost and favorable environmental characteristics. Initially, one of the biggest challenges in converting from an anhydrous formulation (or one with low water content) to an aqueous system was achieving equivalent product performance and quality. However, as the transition to water-based formulas takes place, corrosion control is another major challenge. Corrosion can be quite tenacious and can occur in aluminum as well as tinplate cans.

In recent years, one way to meet VOC reductions and avoid water-related corrosion problems was to formulate anhydrous systems using HFC-152a. Now, with increasing pressure to further reduce VOC levels in aerosol products, water is being considered for HFC-152a systems as well. When combating corrosion problems, some formulators have had success by modifying the aerosol package. Others have investigated and optimized corrosion inhibitor systems. As part of the technical support for its propellants, Chemours conducts laboratory studies to help customers screen the effectiveness of different corrosion control options for aerosol products.

Past work focused mainly on HP DME (dimethyl ether), because it was one of the primary propellant choices for aqueous systems. HP 152a has typically been used in anhydrous systems; but, now as that changes, recent studies have evaluated corrosion inhibition for aqueous HP 152a formulations as well.

Aerosol Container Materials

Many formulators who experience difficulties with corrosion in tinplate containers attempt to use aluminum cans to alleviate the problem. Unfortunately, aluminum containers can also be susceptible to corrosion. Aluminum is known to resist corrosion in some cases, because of its ability to form an aluminum oxide layer on the surface of the metal. This layer can be a very effective barrier between the metal surface and aqueous environment. But aluminum oxide is soluble in both acidic and alkaline systems. When exposed to either environment, the layer will dissolve and the metal will typically corrode. It follows that a parabolic relationship exists between corrosion rate and pH as illustrated in Figure 1, and that a pH range exists in which the aluminum oxide layer can form and effectively act as a barrier to corrosion.

An oxide layer can also be formed in tinplate containers. Such oxides are soluble in acids, but insoluble in alkalis. Figure 2 illustrates the relationship between pH and corrosion rate in tinplate cans. As pH increases, the oxide layer is permitted to act as a barrier to the aqueous environment, and the corrosion rate typically falls. However, because the layer is soluble in acidic systems, corrosion rate is typically high at low pH.

Figure 1. pH Effects on Corrosion of Aluminum Cans

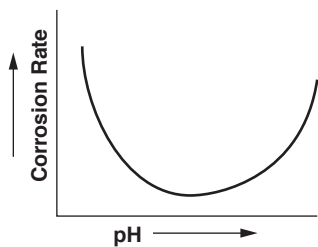
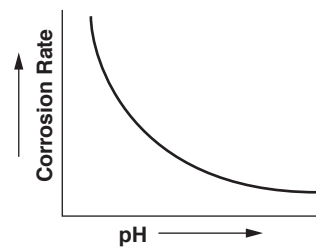


Figure 2. pH Effects on Corrosion of Tinplate Cans



Evaluating Corrosion Control Options

Our laboratory uses both a galvanic corrosion test and an oven aging test to assess effectiveness of different options for corrosion control. This testing can evaluate options that study:

- Solvent/propellant systems alone (no active ingredients)
- Full product formulation
- Different can materials (tinplated steel or aluminum)
- Corrosion inhibitors

This technical information focuses on results of these studies, to date, for HP 152a systems in unlined tinplate steel cans.

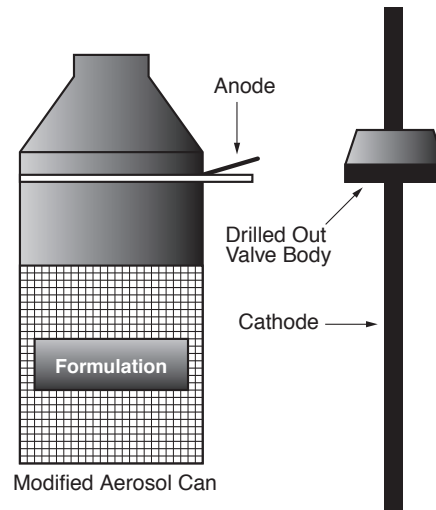
The objective of these tests is to screen potential corrosion inhibitors for aqueous HP 152a-based aerosol products. Results summarized here are for corrosion inhibitors tested in solvent/propellant systems. Work continues on different systems and can materials, and on prototype formulations, as well.

Experimental Details

Galvanic Corrosion Test Unit

Corrosion studies begin with a galvanic corrosion test unit. The unit that was developed is used to induce corrosion in aerosol cans that have been loaded with prototype propellant formulations. The test allows the complete aerosol formulation, including the propellant, to be tested for corrosion. Figure 3 shows a modified tinplate container used to form the galvanic cell. A metal wire or metal hose clamp is wrapped around the can body just below the dome and represents the anode. A stainless steel electrode is inserted in the valve body in place of a dip tube and represents the cathode. Because there is no dip tube, cans are loaded by cold filling. The modified valves are hand-cripped onto each can. A DC power supply is then connected to each can to begin the electrochemical process.

Figure 3. Galvanic Test Cell

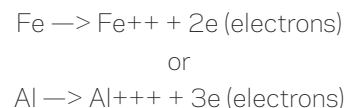


The DC power supply induces the flow of electrons from the anode to the cathode. Because the metal wire is in direct contact with the outer wall of the can, the entire can wall becomes the anode. Concurrently with the electron flow, positive metal ions leave the anode and are oxidized, resulting in the final corrosion product observed; i.e., rust.

Results from the galvanic unit are only used to select formulations for long-term testing and do not represent final stability performance. In most cases, a formulation that corrodes in the galvanic tester will corrode in oven or shelf stability testing; but, lack of corrosion in the galvanic tester does not necessarily indicate a stable system. Such formulations can and have corroded in long-term testing. The galvanic test is, therefore, only used as a screening tool for selecting formulations for long-term testing.

Nature of Corrosion

The process of corrosion is electrochemical in nature and illustrated in Figure 4. The liquid contents represent an electrolyte, and there are anodic and cathodic sites on the can wall. The reaction at the anodic sites is the oxidation of the metal, for example:

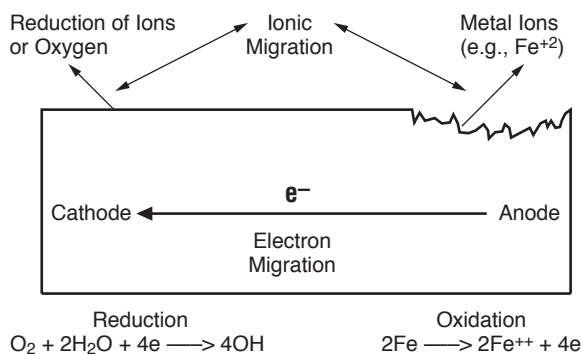


The oxidized form of the metal appears as the corrosion product. The electrons resulting from the oxidation reaction migrate through the metal to the cathode, where they take part in a reduction reaction, such as:



These are just examples of possible reactions. Typically, acidic solutions are "better" electrolytes, allowing ionic migration to take place relatively easily and resulting in more pronounced corrosion effects.

Figure 4. Corrosion Cell



Oven Aging Testing

Although nothing can replace stability testing under the conditions that a product will be used, storage at elevated temperatures usually accelerates corrosion reactions. Oven storage is a common tool for evaluating storage stability, and testing temperatures typically range from 37-49°C (100-120°F).

Results of galvanic and oven testing are summarized by three parameters (see Tables 3 and 4 for examples). These are designated as:

A, B, C

"A" represents an overall assessment of can corrosion on a scale of "0" to "5", with "0" indicating no corrosion and "5" indicating severe corrosion. Slight detinning of the can is given a rating of "2".

"B" represents the condition of the can wall, bottom, and dome (including the mounting cup), and is rated "0" for no corrosion, "+" for the presence of corrosion, and a blank space for slight, but not significant, corrosion.

"C" represents the condition of the bottom joint, dome, mounting cup joints, and the side seam, and uses the same rating system as parameter "B".

Formulation and Inhibitor Testing

Recent work has focused on ethanol/water systems propelled with the following propellants:

- HP DME (dimethyl ether or DME)
- HP DME/hydrocarbon blends
- HP DME/152a (HFC-152a)
- HP 152a

No active ingredients have been used, so that inhibitor systems can be developed for any product category. This testing has also focused on VOC levels of 80 and 55% by weight, which correspond to the California limits for hairspray products. This product category has had the most activity to date, evaluating effective corrosion inhibition options. Table 1 lists the control systems formulations that are used for inhibitor testing. Previous papers (see references) have summarized results for all the formulations; this paper focuses specifically on results for formulation 6, the HP 152a system. Table 2 lists the corrosion inhibitors tested. To provide performance information for different chemical families, and options for different product categories, a broad range of candidates were tested recognizing that not all of these candidates are useful for personal care products. In Table 1, formulation 1 (33% water, 33% ethanol, 34% HP DME by weight) represents the "reference control" used for all corrosion testing done at the laboratory, because it is one known to corrode under nearly all conditions.

Table 1. Control Systems Formulations

	1	2	3	4	5	6	7
Ethanol	33	50	55	25	38	55	55
Water	33	20	20	45	37	15	20
HP DME	34	30	—	30	—	—	—
HP DME/A-31 50/50	—	—	25	—	—	—	—
HP DME/152a (68/32)	—	—	—	—	25	—	—
HP 152a	—	—	—	—	—	30	—
HP DME/A-31 (60/40)	—	—	—	—	—	—	25
% VOC	Reference control	80	80	55	55	55	80

Table 2. Corrosion Inhibitors

Inhibitor	Chemical Name
Ammonium Benzoate	Same
Ammonium Hydroxide	Same
Cyclohexylamine	Same
Diethylamine	Same
Monacor BE	MEA-Borate and MIPA-Borate
Morpholine	Same
Virco-PET 20	Amine Salts of Octylphenyl Acid Phosphate
Aminomethyl Propanediol (AMPD)	Same
Monacor 1000	Capryloamphoproniate
Triisopropanolamine (TIPA)	Same
Triethanolamine	Same
Witconol 14	Polyglyceryl-4 Oleate
Zonyl™ FSP	Anionic Fluorosurfactant
Hamosyl O	Oleoyl Sarcosine
Nitromethane	Same
Urea	Same
Alkaterge T-IV	Tetraethoxyl Oleyl Oxazoline
Elfugin AKT	Organic Phosphate Ester
Hamosyl L-30	Sodium Lauroyl Sarcosinate
Propylene Glycol	Same
Bentone GEL TN	Benzoate
Potassium Hydroxide	Same
Sodium Benzoate	Same

Galvanic and oven testing results for the formulation 6 are shown in Table 3. Each formulation was tested with 1 wt% inhibitor added (except for sodium benzoate, as noted). Although 1% is a rather high level of a corrosion inhibitor, it enables the formulator to reduce the level of effective inhibitors from 1% until an optimum level is found.

The results in Table 3 are grouped by performance of the corrosion inhibitor in the HP 152a system.

Corrosion inhibitors in Group 1 show good corrosion inhibition in both galvanic and oven tests.

Corrosion inhibitors in Group 2 show good corrosion inhibition in the galvanic test, but show evidence of corrosion in the oven test. In this group, however, the observed corrosion in the oven test was in the vapor area of the aerosol container. This suggests that using a second vapor phase inhibitor with these candidates could provide an effective corrosion inhibitor combination.

Corrosion inhibitors in Group 3 controlled corrosion well in galvanic testing, but, as yet, have not undergone oven testing. These remain potentially effective inhibitors; but, oven testing is required to draw further conclusions.

Corrosion inhibitors in Group 4 are compounds that have had some effect in reducing the corrosion in either the liquid or vapor areas of the container. These candidates may potentially be combined with an appropriate second inhibitor to provide an effective inhibitor combination, but additional testing is required.

Corrosion inhibitors in Group 5 are candidates that appear to be ineffective in aqueous HP 152a systems. In these cases, corrosion generally occurred throughout the entire container.

In evaluating the efficacy of corrosion inhibitors, testing parameters must be kept in perspective. For example, the concentration of any inhibitor has an effect on performance. A case in point is sodium benzoate. At a 1 wt% addition level, sodium benzoate was not an effective corrosion inhibitor as judged from galvanic testing. However, when the addition level was reduced to 0.2 wt%, galvanic testing showed that corrosion inhibition improved significantly. Subsequent oven testing at the 0.2 wt% level showed good inhibition performance in the liquid phase, suggesting that a vapor phase inhibitor could complement sodium benzoate.

A second point to be made is the effect of formulations on inhibitor performance. The best HP 152a performers were tested in the other control formulations, and the results are summarized in Table 4. As can be seen, corrosion inhibitors will perform differently depending on the formulation.

These points are highlighted simply to frame the usual caution: these testing techniques offer enormous value in screening and prioritizing inhibitor candidates, but ultimately, a chosen additive has to be tested in the final product formulation.

Chemical Corrosion Control

Two ways to chemically control corrosion include maintaining the pH at the appropriate level or adding inhibitors. Control of pH can be very effective, but, it is not uncommon that the pH required for corrosion control results in poor product performance. For example, a particular hairspray formulation may not be corrosive if the pH is increased to 9.0 or 9.5. However, such high levels could have adverse effects on the resin and, consequently, the product's hair-fixing ability.

When selecting a corrosion inhibitor, it is important to consider potential effects of the inhibitor on product performance, as well as effects on the person using the product. For example, early corrosion work by Chemours indicated that several amine phosphates, such as DMA-4, RP-2, and AFA-1, can be effective at inhibiting corrosion. These compounds are typically used as fuel additives. Although the nature of these compounds may make them appropriate for certain industrial products, toxicity studies on them are insufficient to allow their use in personal care applications.

There are several different types of corrosion inhibitors, two of which are passivating and filming inhibitors. Passivating inhibitors are also, known as oxidizers. Most act by “passivating” anodic sites and include phosphates and silicates. Filming inhibitors form barriers between the metal surface and the aqueous environment and can be organic or inorganic. Organic filming inhibitors are long chain molecules with a polar end that adsorbs on the metal surface and an organic end that is presented to the aqueous environment to repel it. Examples of such inhibitors are amines. Inorganic filming inhibitors precipitate an insoluble layer on the surface of the metal and include compounds such as bicarbonates and phosphates.

Table 3. Corrosion Inhibitor Test Results for HP 152a Systems

Group	Inhibitor ^a	Galvanic Test				Oven Test				Comments		
		Rating			Area of Corrosion ^b	Rating			Area of Corrosion ^b			
		A	B	C		A	B	C				
	None	2	+	+	L	V	3	+	+	L	V	Reference Control
1	Ammonium Benzoate	0	0	0			0	0	0			Good performance in both tests
	Ammonium Hydroxide	0	0	0			0	0	0			Good performance in both tests
	Cyclohexylamine	0	0	0			0	0	0			Good performance in both tests
	Diethylamine	0	0	0			0	0	0			Good performance in both tests
	Monacor BE	0	0	0			0	0	0			Good performance in both tests
	Morpholine	0	0	0			0	0	0			Good performance in both tests
	Virco PET 20	0	0	0			0	0	0			Good performance in both tests
2	AMPD	0	0	0			2	+	+		V	Potential for adding vapor phase inhibitor
	Monacor 1000	0	0	0			2	0	+		V	Potential for adding vapor phase inhibitor
	Sodium Benzoate at 0.2 wt%	0	0	0			2	+	0		V	Potential for adding vapor phase inhibitor
	TIPA	0	0	0			3	0	+		V	Potential for adding vapor phase inhibitor
3	Triethanolamine	0	0	0								Oven testing needed
	Witconol 14	0	0	0								Oven testing needed
4	Zonyl™ FSP	2	0	+		V	2	+	+		V	Potential for dual inhibitors
	Hamposyl O	2	0	+		V						Potential for dual inhibitors
	Nitromethane	4	+	+	L							Potential for dual inhibitors
	Urea	3	+	0	L							Potential for dual inhibitors
5	Alkaterge T-IV	3	0	+	L		3	+	+		V	Did not inhibit corrosion
	Elfugin AKT	3	+	0	L		3	+	+		V	Did not inhibit corrosion
	Hamposyl L-30	4	+	+	L	V	4	+	+	L	V	Did not inhibit corrosion
	Propylene Glycol	4	+	+	L	V	4	+	+	L	V	Did not inhibit corrosion
	Bentone GEL TN	4	+	+	L	V						Did not inhibit corrosion
	Potassium Hydroxide	5	+	+	L	V						Did not inhibit corrosion
	Sodium Benzoate	5	+	+	L	V						Did not inhibit corrosion

^aAt 1 wt%, unless otherwise specified.

^bL = Can corrosion in liquid phase; V = can corrosion in vapor phase.

Notes

- Corrosion rating system is described in Table 4.
- Galvanic tests were run in galvanic corrosion test unit.
- Oven tests were run at 49°C (120°F) for up to 3 months.

Table 4. Corrosion Inhibitor Test Results for HP 152a and HP DME Systems

Formulation #	2			1			4			6			5			7			3		
Formulation Composition, wt%	Ethanol = 50 Water = 20 DME = 30			Ethanol = 33 Water = 33 DME = 34			Ethanol = 25 Water = 45 DME = 30			Ethanol = 55 Water = 15 152a = 30			Ethanol = 38 Water = 37 DME/152a = 25 (68/32 DME/152a)			Ethanol = 55 Water = 20 DME/A31 = 25 (60/40 DME/A31)			Ethanol = 55 Water = 20 DME/A31 = 25 (60/40 DME/A31)		
Rating	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
No Inhibitor	3	+	+	4	+	+	4	+	+	3	+	+	4	+	+	4	+	+	4	+	+
Ammonium Hydroxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Diethylamine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Virco-PET20	0	0	0	0	0	0	2	0	+	0	0	0	2	0	+	0	0	0	0	0	0
Cyclohexylamine	0	0	0	2	+	0	2	+	0	0	0	0	2	+	0	2	+	0	2	+	0
Morpholine	0	0	0	3	+	+	2	+	+	0	0	0	3	+	0	0	0	0	0	0	0
Ammonium Benzoate	2	+	0	2	+	0	2	+	0	0	0	0	2	+	+	0	0	0	0	0	0
Monacor BE	0	0	0	2	0	+	2	+	+	0	0	0	2	+	+	2	0	+	2	0	+

Corrosion Rating System

A*	B	C
0 – No corrosion	Can wall, bottom, and dome	Bottom joint, dome joint, and side seam
1 – Mild/little attack		
2 – Mild/significant**	0 – No corrosion	0 – No corrosion
3 – Moderate corrosion	+ – Corrosion present	0 – Corrosion present
4 – Heavy corrosion	Blank – Slight, but not significant, corrosion	Blank – Slight, but not significant, corrosion
5 – Severe corrosion		

*This numerical rating is an overall assessment of the total can (tinplate, joints, and side seams) and represents the primary rating of a test. A rating of 1–2 is considered effective and >3 is a failing rating.

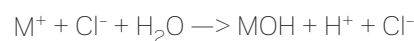
**Slight detinning of test cells is given a rating of 2.

Note: Tests were run using unlined tinplate steel cans with 1 wt% inhibitor oven-aged up to 3 months at 49°C (120°F).

Other Considerations

An important consideration, once an effective corrosion inhibitor has been identified, is the presence of potential decomposition products. Such compounds need to be evaluated, not only from the standpoint of their performance as inhibitors, but also from their ability to decompose into something that could, in turn, affect container stability or product performance. Such studies should be conducted in conjunction with long-term container stability testing, once a potential inhibitor has been selected.

Chloride ions have been the topic of many stability studies and can impact even the best plans for corrosion control. These ions can be very aggressive in breaking down protective films or in preventing their formation. The reaction once the metal (M) is exposed is typically hydrolysis in water:



The MOH can also form metal oxide and is manifested as rust. Although corrosion can take place in the absence of chloride ions, their presence, from the water used or as an impurity in formulation components, can have a catalytic effect on the rate of corrosion.

Summary

Corrosion control has been a challenge to the introduction of many water-based aerosol formulations. Some marketers have met the challenge with certain formulations by altering the packaging system or by adding inhibitors to their formula. However, to date, there is no single solution that can be applied to all types of products. Thorough corrosion inhibition testing is required to ensure that a safe, stable product is developed. Screening tools and short-term testing are all effective ways to assist in this testing; but, nothing can replace final product storage stability testing for evaluating efficacy of corrosion inhibitors.

Chemours conducts both galvanic and oven stability testing for water-based formulations that use our propellants. For additional information, please contact your Chemours representative.

References

"Corrosion in DME/Water Aerosol Systems - Parts 1-4,"
Dr. Lynn Applegate.

"Corrosion Inhibitors for Water-Based Aerosol Systems,"
Maria Boulden.

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