

Epoxy curing agents for high temperature-high pressure chemical resistant coatings

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ABSTRACT

Epoxy coatings can be found in a broad range of industries and applications due to their exceptional performance such as corrosion and chemical resistance, mechanical properties, and adhesion to wide range of substrates. Within the protective coating market, epoxy systems have been used for many years as linings inside of chemical storage tanks, vessels and pipelines due to their good thermal and chemical resistance properties. In the petrochemicals industry, high-solid epoxy coatings are also used for lining rail cars that transport crude oil. Specific to the petrochemical industry where facilities handle both conventional crude or shale crude, the requirements placed on the coatings are extremely demanding since quite often the coatings are exposed to highly corrosive chemicals and gases such as hydrogen sulfide, sulfuric acid, and carbon dioxide at both elevated temperatures and pressures. To better serve the petrochemical sector coating manufacturers need linings which provide a high level of chemical resistance and pass stringent industry standards. In addition, there is a requirement in the protective coatings market to develop chemical resistant epoxy tank linings that can provide excellent resistance to a range of alcohols, solvents, alkali, and diluted acids stored at elevated temperatures. In this paper we will discuss how a design of new epoxy curing agents with an improved chemical resistance can help formulators to meet these increasing industry needs. The model formulations and application performance properties such as, immersion service test data, high temperature-high pressure autoclave and Atlas Cell test data will be discussed and summarized.

Key words: Crude oil, Corrosion, Chemical resistance, hydrogen sulfide, high temperature, high pressure, Sulfuric acid.

INTRODUCTION

The crude oil produced by fracking or hydraulic fracturing method are high in sulfur content (0.5%)¹. The vast majority of vessels that are used in the petrochemical industry to store and transport materials are constructed using Carbon steel. Coating linings used for corrosion protection inside of vessels and tanks must perform under severe conditions such as an exposure to corrosive gasses (H₂S) and carbon dioxide as well as high temperatures, high pressures and often must withstand the cold wall effect and rapid decompression.

Sulfuric acid is an essential industrial chemical with most of it used in manufacturing of fertilizers, industrial detergents, and batteries. The concentration of sulfuric acid used for these applications range from less than 30% and as high as 98%. Sulfuric acid is a powerful oxidizer and requires specialty materials for transportation and storage. The specialty materials such as poly-tetra-fluoroethylene (PTFE) coatings are cost prohibitive and very difficult to repair in case of damage². Two component epoxy coatings that resists swelling and diffusion and subsequent degradation of epoxy amine crosslink network at ambient and elevated temperature are ideal for such a demanding application. The chemistry and network structures are vital in influencing the resistance of a coating to sulfuric acid.

Two-component amine cured epoxy systems are thermoset polymers and have a long history of success in the ambient environment chemical resistant coatings market. These formulations typically consist of formulated epoxy resin on the A side and the amine curing agent on the B side. In the petrochemical coatings market and other applications that require ultra-high chemical resistance, the epoxy resin choices are limited to Bisphenol A diglycidal ether (Bis A resin), Bisphenol F diglycidal ether (Bis F resin) and multi-functional Epoxy Novolac resins. While the epoxy resin structure and reactivity is important, it's a selection of amine curing agent that plays the dominant role for applications that require enhanced resistance to high temperature, high pressure, and aggressive chemical environments. This paper will detail the significant role amine curing agents play in coatings that require high chemical resistance to a) aggressive environments under high temperature/high pressure and b) 98% sulfuric acid at elevated temperatures.

EXPERIMENTAL PROCEDURE

Materials used for studies

Chemicals structures of amines used in curing agent formulations are given below in Figure 1. The physical properties of the epoxy resins are given in Table 1. Amine curing agents and respective formulations that were used for high temperature application tests are given in Table 2 and 3. Amine curing agents with corresponding coating formulations for 98% Sulfuric acid testing are provided in Table 4.

Figure 1: Chemical structures of the amines used in formulations for curing agents

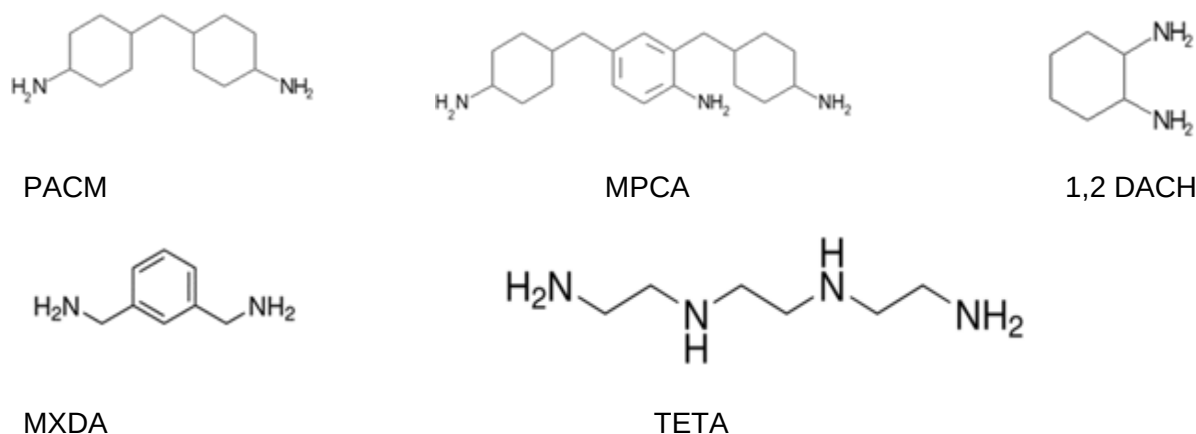


Table 1 Physical properties of epoxy resins

Properties	Epoxy Novolac Resin	Bis F Epoxy Resin	Bis A Epoxy Resin
Epoxide eq wt. (g/eq)	176-181	167-174	185-192
Color (Gardner)	2 max	2 max	2 max
Viscosity@ 25°C	1200-2000	3400-4200	1100-14000
Functionality	3.6	2	2

Table 2 Amine curing agents used for Coatings testing at high temperature and high pressure Autoclave and Atlas cell testing.

Curing Agents	Amine Description	AHEW
CA-A	MPCA	110
CA-B	MPCA- PACM	54
CA-C	MXDA	49
CA-D	1,2- DACH	90
CA-E	1,2- DACH	96

Table 3 Coatings for testing by Autoclave and Atlas Cell – 2 coats with DFT 17-20

Coating ID	Epoxy Resin Type	Curing Agent Type
EN-1	Epoxy Novolac	CA-A
EN-2	Epoxy Novolac	CA-B
EN-3	Epoxy Novolac	CA-C
EN-4	Epoxy Novolac	CA-D
EN-5	Epoxy Novolac	CA-E
BF-1	Bisphenol F	CA-A
BF-2	Bisphenol F	CA-B
BF-3	Bisphenol F	CA-C
BF-4	Bisphenol F	CA-D
BF-5	Bisphenol F	CA-E
BA-1	Bisphenol A	CA-A
BA-2	Bisphenol A	CA-B
BA-3	Bisphenol A	CA-C
BA-4	Bisphenol A	CA-D
BA-5	Bisphenol A	CA-E

Table 4 Amine curing agents and castings used for coatings evaluated for 98% Sulfuric acid resistance at elevated temperature

Casting ID	Type	Curing agent	Base Amine	Curing Agent AHEW
F1	Cycloaliphatic adduct	CA-1	1,2, DACH	94
F2	Aliphatic mannich base	CA-2	MXDA	88
F3	Aliphatic mannich base	CA-3	MXDA	110
F4	Formulated cycloaliphatic	CA-4	MPCA	115
F5	Formulated cycloaliphatic	CA-5	PACM	49
F6	Aliphatic adduct	CA-6	TETA	83

AHEW= Amine hydrogen equivalent weight

Application Testing

Autoclave testing (NACE TM-0185) ³

The autoclave testing NACE TM-0185 is the standard test method to determine the suitability of a coating for tank lining applications. The test conditions which include pressure, temperature and fluid- gas mixtures can be preselected to simulate the environmental field conditions. The autoclave testing consisted of three phases: a) aqueous phase -1% sodium chloride b). hydrocarbon phase -toluene/kerosene c) gas phase - mixture of 90% methane, 5% hydrogen sulfide and 5% carbon dioxide. The coatings are applied in two coats to a total dry film thickness of 12-17 mils on both sides of the ASTM A 36 hot rolled Carbon steel panels abrasive blasted to SSPC-SP5/ NACE 1 white metal to obtain sharp angular profile in the range of 2.0 ± 0.5 mm.

Atlas Cell Testing (NACE TM-0174)⁴

The Atlas Cell test method NACE TM-0174 is an immersion test method. The pressurized Atlas Cell test is designed to simulate conditions in pressurized pipelines, treaters, and vessels. It measures the ability of the coating to withstand the temperature gradient between the internal and external surface -cold wall effect- under the influence of the pressure, temperature, and internal environment. The Atlas Cell testing consisted of three phases: a) aqueous phase – 1% sodium chloride b) hydrocarbon phase -toluene/kerosene c) gas phase – Mixture of 90% methane, 5% hydrogen sulfide and 5% carbon dioxide. The coatings are applied in two coats to a total dry film of 12-17 mils on the blasted profile side of the ASTM A 36 hot rolled Carbon steel panels abrasive blasted to SSPC-SP5/ NACE 1 white metal to obtain sharp angular profile in the range of 2.0 ± 0.5 mm

The accelerated laboratory performance testing of model epoxy lining formulations presented in Table 3 was performed on the ASTM A36 hot rolled carbon steel panels abrasive blasted to SSPC-SP5/NACE 1 white metal to obtain sharp angular profile in the range of ± 0.5 mm measuring 7.6" X 7.6 " X 0.125" for Atlas cell test and 6.0" X 3.5" X 0.125" for Autoclave test with an average dry film thickness of 17-20 mils spray applied in two coats. The coatings were cured at ambient temperature and tested at Evonik high temperature/high pressure lab according to NACE TM-0185 and NACE TM-0174 test methods. The test protocols are given in **Table 5**.

Table 5: Test protocol for Autoclave and Atlas Cell testing

	Pressurized atlas Cell	Auto Clave
Test description	NACE TM-0174 NACE TM0174 Evaluation of Protective Coatings and Lining Materials on Metallic Substrates in Immersion Service	NACETM-0185 Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods by Autoclave