Progress in Organic Coatings 77 (2014) 395–402

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Mechanical and anticorrosive properties of non toxic coal-tar epoxy alternative coating

S.D. Jagtap, S.P. Tambe*, R.N. Choudhari, B.P. Mallik

Asian Paints Ltd., Research & Technology Centre, Thane-Belapur Road, Navi Mumbai 400703, India

ARTICLE INFO

Article history:
Received 23 April 2013
Received in revised form 6 October 2013
Accepted 1 November 2013
Available online 8 December 2013

Keywords:
Coal tar
Bitumen
Hydrocarbon resin
Epoxy and flexibilizer

ABSTRACT

Coal tar epoxy (CTE) coating system has been widely used for protection of steel structures under atmospheric, buried and immersion conditions because of their low water vapour permeability, high electrolyte resistance and good antibacterial properties. However, coal tar has been classified as carcinogen, mutagen and toxic for reproduction (CMR) as per International guideline (REACH, IARC and GS 11). It is now banned in the developed nations like US, Europe, Japan, etc. As the use of coal tar is being restricted, there is an urgent need to formulate a coal tar free epoxy product for corrosion protection of structures. In the present study, alternative approaches have been proposed to replace coal tar such as bitumen (BIT), hydrocarbon resin (HR), flexibilizer (FL) and curing agents like polyamide (PAD) or polyamine (PAM). Four different coal tar free formulations were formulated separately by using these approaches. The standard CTE and coal tar free epoxy compositions were evaluated for mechanical properties such as elongation at break, tensile strength, adhesion strength and resistance to abrasion, impact and flexibility. The resistance to corrosion of optimized composition (epoxy-HR-FL-PAD-PAM) and coal tar epoxy coating was evaluated by exposing to different environments. The corrosion resistance property was also evaluated by cathodic disbondment and electrochemical impedance spectroscopy (EIS) technique. Results indicate that epoxy-hydrocarbon resin-flexibilizer composition cured with blend of polyamide and polyamine has comparable mechanical and corrosion protection properties to that of standard CTE.

1. Introduction

The paint systems used for protection of steel structures are being upgraded regularly to comply with the statutory regulations to safety; health and environment and also to respond to emerging new regulations and upcoming changes in those existing regulations [1,2]. The growing awareness and concerns about the environment safety and health in the paint industry has been the most influential driver for new technology development during the last 2–3 decades. To meet the progressive demands for environmental friendly products; existing coatings are being re-engineered suitably to make them eco-friendly.

Coal tar based coatings have been extensively used for protection of steel structures and underground pipe for more than 100 years. Coal tar has also been used to modify several polymeric resin binders such as epoxy, chlorinated rubber, vinyl and polyurethane for enhancing their anticorrosive characteristics. Coal tar epoxy paint coating has been widely used for structures operating in marine environment, especially below water line areas, in view of its extremely low permeability, high electrolytic resistance and good adhesion even on marginally prepared surfaces [3]. The ratio of epoxy resin to coal tar varies based on the desired cost of the formulation as well as essential properties that are intended to be achieved. Coal tar acts as filler within cross linked epoxy matrix which improves the coating in respect of flexibility, toughness, adhesion, UV resistance and high moisture resistance. Coal tar epoxy coatings offer excellent resistance to salt water and cathodic disbondment and hence these are ideally suited for protection of ships submerged hull areas, ballast tank, cooling tower, offshore and harbour installations. The CTE coatings have shown good compatibility when applied on rusted or partially prepared surface.

Coal tar is a heterogeneous mixture of complex polyaromatic hydrocarbons (PAHs), such as xylene, naphthalene and its alkyl derivatives, anthracene oil and other resinous materials [4,5]. Some of these compounds are carcinogenic in nature and are toxic to human health and environment [6–10]. According to the International Agency Research on Cancer (IARC), formulations that contain more than 5% of crude coal tar are categorized as Group-1 carcinogen. National Fire Protection Association (NFPA) states that coal tar contains approximately 10,000 different chemicals, of which only about 50% have been identified and the composition of coal tar varies depending on its origin and type of coal used to make it. Coal tar based coatings are black or brown in colour and do not give good

* Corresponding author. Tel.: +91 22 39153542.
E-mail address: shekhar.tambe@asianpaints.com (S.P. Tambe).

0300-9440/$ – see front matter
http://dx.doi.org/10.1016/j.porgcoat.2013.11.003

Table 1
Composition of CTE and their alternatives with different approaches.

Comp.	Resin/pigment-extender description	Approaches
CTE	Coal tar-epoxy-PAD/steatite	–
1	Epoxy-BIT-PAD/steatite	Bitumen
2	Epoxy-HR-PAD/TiO_2, steatite and barytes	Hydrocarbon resin
3	Epoxy-HR-FL-PAD/TiO_2, steatite and barytes	Hydrocarbon resin and flexibilizer
4	Epoxy-HR-FL-PAD-PAM/TiO_2, steatite and barytes	Polyamide and polyamine curing agent

PAD, polyamide with amine hydrogen equivalent weight: 180.
PAM, polyamine with amine hydrogen equivalent weight: 115.
HR, hydrocarbon resin with hydroxyl value: 55.
FL, flexibilizer.

aesthetic appearance. This also makes application and inspection difficult in the confined areas. Coal tar bleeds into the topcoat leading to change in appearance of the coatings at higher temperature in contact with water.

Due to imminent ban of environmentally harmful coal tar based paint products, development work have been forwarded to use of other material for modification of binders. Limited information [11–15] is available on materials as substitutes of coal tar in protective coating formulations. Bitumen is one of such material that can be used to replace coal tar because polyaromatic hydrocarbon concentrations in bitumen is about 50 mg/kg compared to 100,000 mg/kg in coal tar. Epoxy-modified bitumen has been used as replacement for coal tar as binder to prepare anti-skid surfaces for runways [11,12]. Gaughen et al. [13] developed polysulphide modified epoxy coating as an alternative to coal tar epoxy paint for splash zone area. Modified hydrocarbon resin based formulation developed a coloured tar free epoxy coatings which addressed applicator health and safety concerns [14]. The hydrocarbon resins can be functionalized to obtain carboxylic or phenolic functional groups which enhance compatibility with epoxy resins. Epoxy-hydrocarbon resin have very good penetrating and wetting properties; creating optimized adhesion on ill prepared surfaces. Epoxy functional reactive diluents/plasticizer system react with the curing agents to become the part of the cross-linked epoxy system. These reactive diluents influence the various performance properties such as impact strength; adhesion; flexibility; filler-loading; and solvent resistance as like coal tar based coating. Epoxy-phenalkamine system provides the coating with high hydrophobicity and good adhesion on wet or poorly prepared surfaces as CTE-polyamide system [15].

The objective of present work was to study coal tar alternative formulations through various approaches and to compare their performance against CTE. The alternative anticorrosive coatings should possess good mechanical properties, barrier properties i.e. low water and ionic permeability and also provide superior surface tolerant properties on marginally prepared rusted surfaces. It is also essential that developed system be compatible with the cathodic protection system. In the present work, four compositions were formulated separately using different materials other than coal tar. These were evaluated and compared in respect of their mechanical properties against coal tar epoxy coating. Further, optimized coal tar free composition and CTE were evaluated for their resistance to corrosion by exposing them in different environments.

2. Experimental

2.1. Materials

High molecular weight epoxy resin based on diglicidyl ether of bisphenol-A (DGEBA), EEW-450 was obtained from Huntsman Advanced Materials (Europe). Polyamide (AHEW-180) and polyamine (AHEW-115) hardeners, used as curing agent, are proprietary products of the company. Coal tar (85%, w/w) and bitumen (65% in xylene) samples were obtained from Neptune hydrocarbons Pvt. Ltd. (India). Epoxies terminated blocked isocynate resin (FL, EEW-930) and modified liquid hydrocarbon resin (HR, HV-55), procured from commercial sources, were used as flexibilizers. All pigments and fillers employed for experimental formulations were commercial grade and used without purification. The chemicals and reagents used for testing were of analytical grade.

2.2. Design of formulation and processing

The coal tar epoxy and coal tar free four experimental compositions were prepared as per details given in Table 1. The CTE composition, ratio of coal tar to cured epoxy resin was kept at 60:40 and cured with polyamide (PAD) curing agent. In coal tar free compostion-1 and 2, 30% by wt of coal tar present in standard formula was replaced separately with bitumen and hydrocarbon resin respectively. In order to improve the flexibility, 2% flexibilizer (FL) was incorporated in the composition-3. Compositions 1–3 were cured with polyamide curing agent. With a view to further improve its mechanical and curing properties, composition-3 was cured with a blend of polyamide (PAD) and polyamine (PAM) in ratio of 70:30. All compositions were formulated at 24% pigment volume concentration (PVC) and with stochiometric requirement of curing agent. Being company propriety, details of complete formulation could not be revealed. Paint formulations were processed using table top high speed disperser at 2000 RPM.

3. Characterizations

3.1. Mechanical properties

3.1.1. Tensile properties

Tensile strength and elongation at break of free films of all compositions were determined using Universal Testing Machine (INSTRON, Model-3367) as per procedure described in ASTM D882. Test specimens having average thickness of $200 \pm 10\,\mu m$ were strained at a rate of 20 mm/min.

3.1.2. Pull-off adhesion strength

Adhesion strength of the coatings was determined as per method described in ASTM 4591-09 using Portable adhesion tester (Posi Test AT-A). Paint compositions were applied on mild steel of size 150 mm × 100 mm × 3 mm. These coupons were prepared in two sets; one prepared by grit blasted (Sa 2.5) and other on rusted surface (St 2) at $200 \pm 10\,\mu m$ dry film thickness (DFT). The coated specimens were cured at ambient temperature for 7 days before testing.

3.1.3. Determination of abrasion resistance, impact resistance and flexibility

Abrasion resistance was determined as per procedure described in ASTM D 4060 01 using Taber abrasion testing machine (Model-503). The coated mild steel specimens (DFT $200 \pm 10\,\mu m$; size