

PREPARATION AND EVALUATION OF NEW ANTI-CORROSIVE COATING BASED ON ASPHALT CEMENT (60/70) BLENDED WITH POLYESTERAMIDE RESIN FOR STEEL PROTECTION

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Abstract

The blending of a resin with asphalt cement is a simple method for improving the properties of anti-corrosive paints for the protection of steel. This paper outlines the potential of using asphalt cement blended with polyesteramide resin, for use in paints. Asphalt cement is the most extensively used economic coating material, whereas long polyesteramide resins are predominantly used for air, and force-dry, industrial coatings on metal surfaces. The aim of the research was to blend the two materials together with the objective of reinforcing the positive properties of the resin and attempting to compensate for the resins areas of weakness. The formation of modified functional asphalt cement was based on the fine dispersion of a polyesteramide resin within the asphalt cement, for which the chemical composition of the cement is of key importance. The degree of modification depends on the properties, content and nature of the polyesteramide. The coating blend was characterised using scanning electron microscopy (SEM) and the performance of the coating blend panel was evaluated for mechanical properties and corrosion resistance. The results obtained confirmed that blends of asphalt cement and polyesteramide resin were effective binder materials for industrial coating applications.

Keywords: Polyesteramide blend; Asphalt cement; Asphalt cement blend; Inhibition of steel protection.

1. Introduction

The mechanism whereby an organic coating protects a metallic material from the environment is a complex process that is not well understood. Many properties of polymers such as process ability, electrical, chemical, thermal, mechanical properties and environmental stability, affect their suitability and reliability as protective organic coatings [1]. Corrosion inhibition is generally achieved by the deposition of either, passive films or active conversion coatings, onto the surface of the material requiring protection. These coatings may offer a low density of pores, or cause

surface chemical reactions, in order to prevent oxidation [2-6]. A survey of the literature reveals that the protection offered by an organic coating can be ascribed to one of the following mechanisms: (i) depression of the anodic and/or cathodic reaction; (ii) introduction of a high electrical resistance into the circuit of the corrosion cell; and (iii) as a barrier to aggressive species such as oxygen, water and ions [7-10]. Performance evaluation of a high durability asphalt binder and a high durability asphalt mix for the wearing course of bridge deck pavement were studied [11]. Bitumen with synthetic polybutyl acrylate was found to be considerably softer, and more viscous in nature at ambient temperature, compared with conventional bitumen, leading to synthetic polymer binders being combined with penetration grade bitumen to produce bitumen/synthetic binders and combined synthetic binder blends [12]. Today, polyesteramide resins surpass all other synthetic coating resins used as binders in the surface coatings industry. The term “modified polyesteramide” is used to describe products obtained by chemical modification [13]. New anti-corrosive coating compositions based on long alkyd resin were prepared and characterised as having high gloss, good adhesion and a high degree of flexibility [14].

The blend of short oil-length alky resin with coal tar resulted in better coating properties. The coating blends were studied using SEM, and were found to offer very good corrosion resistance when exposed to a salt spray environment. The coating blends also exhibited very good mechanical properties such as adhesion, flexibility and scratch hardness due to the blends being a combination of thermosetting and thermoplastic resins. The use of tar gives the alkyd resin formulation certain benefits such as high flexibility and high water resistance. Coal tar has a high resistance to moisture and good adhesion to steel. Thus they are very suitable for structures that are immersed in water or burial underground, and the incorporation of alkyd resin improves the coal tar drying time, gloss level, scratch hardness and chemical/corrosion resistance [15]. In the present study, polyesteramide resin was blended with asphalt cement. It was expected that polyesteramide resin will further improve the performance characteristics of the finishes asphalt cement resin.

2. Experimental

2.1. Materials

The linseed oil fatty acid “LOFA” was used supplied by Akzo Nobel of the Netherlands. The phthalic anhydride “PA” was used a product of Avondale laboratories in England. The glycerol (G), sulphuric acid, anhydrous sodium

carbonate, benzene, glacial acetic acid, diethanol amine and ethyl acetate were all supplied by the El Nasr Pharmaceutical Company in Egypt. The xylene and mineral turpentine were supplied by the Misr Petroleum Company in Egypt. The asphalt 60/70 cement was obtained from the Suez Oil Processing Company. The technical data for this material is shown in Tables 1, 2 and the used blended composition is represented in Table 3.

2.2. Formation of dihydroxy - diethylamide derivative of linseed oil fatty acids [HELA]

A mixture of freshly distilled diethanolamine (DEA) (11.55g, 0.11mol) and linseed oil fatty acid (28.0g, 0.1mol) was added to a 250 ml round-bottom flask, fitted with a Dean and Stark trap. The mixture was allowed to reflux in the presence of 15% xylene until the theoretical amount of water (1.8 ml, 0.1mol), was collected, indicating the complete formation of N,N-bis (2-hydroxyethyl) linseed oil fatty acid amide (HELA). Reaction diagram 1.

2.3. Synthesis of long oil-length polyesteramide resin

Polyesteramide resins were prepared through a condensation polymerisation reaction via a solvent process, in a one stop reaction. A mixture of a calculated amount of hydroxyl ethyl linseed oil fatty acid amide (HELA) as the ingredient source of the polyol, and phthalic anhydride (PA) as the ingredient source of the polybasic acid, was added to a 250 ml round bottom flask fitted with a Dean and Stark trap. The ingredients were refluxed in the presence of 10% xylene solvent. The course of esterification was followed by observing the theoretical amount of water liberated. It should be noted that within each set of formulations, the total number of acid and hydroxyl equivalent, for the various individual runs, was kept constant. Resin characteristic constant and weight changes associated with the various formulations are shown in Table 4. Alkyd polyesteramide calculations can be used to predict the completed formulation, properties of the resin, the amount of reaction water liberated, and the probable risk of gelation. The calculation of water evolved is also useful, both as a tool for following the course of the esterification reaction and to find the theoretical yield. Reaction diagram 2.

Table 1: Physical properties of used asphalt

Physical Properties	Asphalt Cement(60/70)
Penetration@25°C,0.1mm	63.0
Softening Point, °C	47.0
Flash Point Open Cup, °C	280
Ductility @ 25°C, cm	+100

Table 2: Physical properties of used asphalt

Physical Properties		Asphalt Cement(60/70)
Oil % by wt.		37.4
Resins % by wt.		49.0
Asphaltene		13.3

Table 3: Mixed drier composition.

Composition	Lead	Cobalt	Calcium	Barium	Tall oil	Mineral turpentine
%	26.64	03.28	08.20	10.00	0.82	51.06

Table 4; Formulation polyesteramide resin.

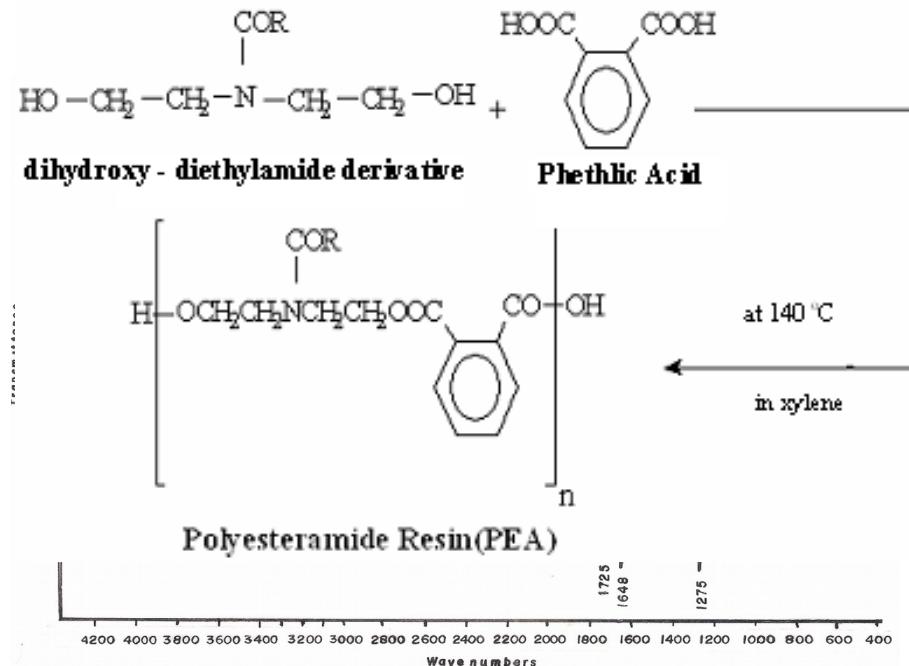
Ingredients	e_o	e_A	e_B	E	F	$W = E e_o$	$m_o = e_o/F$	$R = e_B/e_A$	K = m_o/e_A	H_2O Liberated (ml)
HELA (1.00)	0.260	—	0.260	184.0	2	47.8	0.130	1.00	1.00	2.3
PA	0.259	0.259	—	74.1	2	19.2	0.130			
Total		0.259	0.260				0.260			

e_o : Total Equivalents Present at the Start of Reaction, e_A : Number of Acid Equivalents, e_B : Number of Hydroxyl Equivalent, E: Equivalent Weight, F: Functionality, W: Weight, m_o : Total Moles Present at the Start of Reaction, R: Ratio of Total - OH Groups to Total- COOH Groups (e_B / e_A) and K: Alkyd Constant (m_o / e_A).



Linseed oil fatty acid (LOFA)	Diethanol amine (DEA)	N, N-bis (2-hydroxyethyl) linseed oil fatty acid amide (HELA)
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Reaction Diagram 1:

**Reaction Diagram 2:****Fig. 1: IR Spectra of polyesteramide resin**

2.4. Blend of asphalt cement with long oil-length polyesteramide resin

The asphalt cement was used in solid form and required breaking into small pieces. Any of the pieces polluted by soil, water, grease or similar matter were removed. The asphalt cement heating kettle, complete with lid, was equipped with an accurate and easily read thermometer and a mechanical stirrer. The asphalt cement was thoroughly melted and brought up to the application temperature. The material was then sieved using a scarab filter, followed by mixing with the polyesteramide resin in different mixing ratios, as represented in Table 5.

2.5. Preparation and evaluation of coating blends

The asphalt cement and the prepared polyesteramide resin were thinned to 50% using xylene and 5% of mixed drier (represented in Table 3) was added to accelerate the reaction of the fatty acid residues (via the double bonds of the resin molecules) with atmospheric oxygen. The resulting coating system was then applied to pre-treated steel panels. The thickness of the coating was approximately 90 μm . The coated glass panels (25 x 75mm) were sealed using paraffin wax around the edges, and then immersed to half their length in the test solution. The drying procedure of the samples, in terms of touch dryness determination, was undertaken using a 100 x 150mm glass plate [16]. The same glass plate was also used to measure the degree of gloss, which was undertaken using a gloss meter at a 60° measuring angle [17]. The film hardness was carried out using the pencil test method [18]. The coating thickness measurements [19], the corrosion resistance measurements [20-23], and the mechanical resistance measurements for adhesion [24] and flexibility [25], were all undertaken on the coated steel panels [26].

2.6. SEM analysis

A Jeol JSM-5500LV scanning electron microscope was used to record the electron micrographs of the coating blend cross-sections.

3. Results and discussion

Polyesteramide resins were made by condensation polymerisation of polyols and polybasic acids. Polyesteramide is composed of phthalic anhydride (difunctional), N, N-bis(2-hydroxyethyl) linseed oil fatty acid amide (HELA). The types of fatty acid used were important in determining the final drying characteristics of the material, since they dry like an oil paint, through auto-oxidation reactions following solvent evaporation [27]. Alkyd polyesteramides were classified by 'oil length', i.e.

the weight percent of oil, or triglyceride equivalent, or fatty acids in the finished resin, or oil. Varying these two factors has a great impact on the final properties of the material, and hence the ultimate application. Alkyd polyesteramide resins are traditionally classified as short, medium, long and very long oil alkyds, with oil content of 35-45%, 46-55%, 56-70% and greater than 70% respectively [28]. The fatty acid portion imparts a number of important properties to the resin, including crosslinking potential, flexibility, compatibility with solvent systems, and control of solubility. In the present work the polyesteramide resin was blended with asphalt cement to yield a coating blend specific for industrial applications.

3.1. Spectral analysis of polyesteramide resin

Structural features of polyesteramide resin were confirmed by Fourier Transform infrared spectroscopy and are represented in Figure 1 show peaks at 3398 cm^{-1} (-OH groups), at 2930 cm^{-1} (C-H) CH symmetric stretching), 2852 cm^{-1} (asymmetric stretching), at 1648 cm^{-1} (CON amide carbonyl) and at 1725 cm^{-1} (COO ester carbonyl stretching), are all typical of a polyesteramide resin. Also present on the spectra are C-H bending, C-O and C-C stretching fingerprint peaks. These are found specifically at 1275 cm^{-1} (strong and rounded, possibly due to the esters), 1134 cm^{-1} , 1071 cm^{-1} (unsaturated aromatic in plane deformation) and at 857 cm^{-1} and 713 cm^{-1} (due to aromatic out of plane bending). These peaks were attributed to the polyester section of the polyesteramide resin.

3.2. Morphology study

Figure 2 illustrates the SEM electron micrographs associated with the study. These were four individual panels. The first panel refers to the raw asphalt cement and the other three panels refer to the coating blend (raw asphalt with 6, 9 and 12% polyesteramide resin). As the morphology indicates, it can be observed that the polyesteramide and asphalt cement are seen to be compatible. The electron micrographs indicate that the asphalt cement has penetrated into the microstructure of the polyesteramide resin, indicating that the mixing procedure of the asphalt cement and resin has been successful.

3.3. Physical-mechanical characteristics of coating blends

Table 6 shows the physical and mechanical results were obtained for the coated film blends. The data shows that, the colour of the coating blends (>18) is dark brown due to the presence of the nitrogenous base. The air drying time was decreased with increased modification. The gloss and scratch hardness were

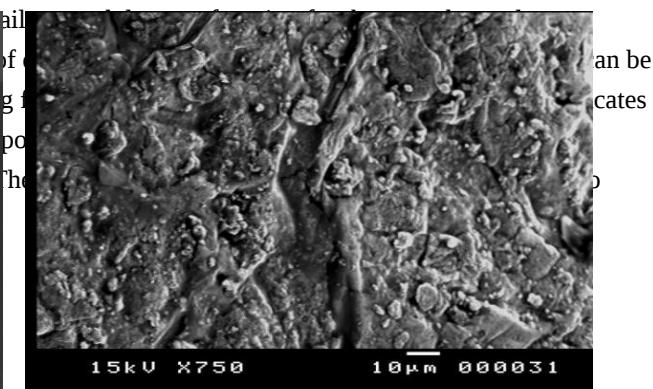
increased with higher levels of polyesteramide resin content. The improvement in the drying properties of the coating blend could possibly be due to the fast drying properties associated with the polyesteramide resin, with reducing the drying time from an initial 24 hours to 7 hours. The results of the pencil hardness test of the various coatings indicate that the coating resistance towards scratching increases with increased amount of polyesteramide resin content. It is the presence of the ester repeat units (-COOR) in the polymeric chain of the oil-based polyesteramide resin that enhance the hardness of the coating blend, in addition to improving both ease of application and faster drying properties. No de-lamination or detachment of the blend coatings were observed, either at the edges or within the square lattice. It is clear that the wet ability of the pre-treated mild steel substrate by the coating blend is good, which is a key factor for the improved adhesion of the coating to the substrate; which could possibly be attributed to the incorporation of drying oil in the coating blend. The flexibility test for the coated panel was undertaken at the mandrel diameter of 6mm, and the test showed no indication of either film cracks or de-lamination. The high flexibility of the coating blend can be attributed to the final resin being composed of a polyester backbone, with its own highly branched polymer and dangling fatty acids, which serve to reduce the level of cross-linking and hence create a more flexible polymer.

3.4. Chemical resistance of coating blends

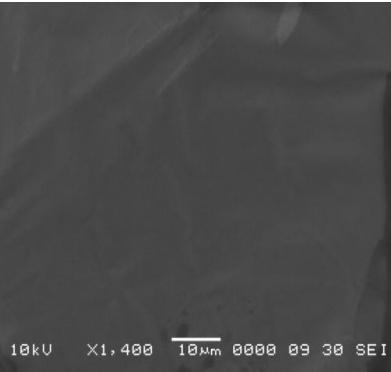
The results presented in Table 7 indicate that all of the samples (A-E) exhibited excellent resistance to both water and acid. However, the coating blend films were slightly affected by the alkali treatment and also showed poor resistance to various solvent media, which could well be attributed to the poor resistance of asphalt cement to hydrocarbons.

3.5 Corrosion resistance of coating blends

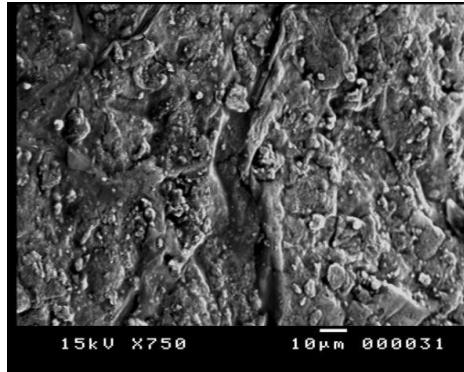
The performance of the coated panels regarding corrosion resistance was evaluated by exposing them in a salt-spray cabinet. The degree of blistering (size



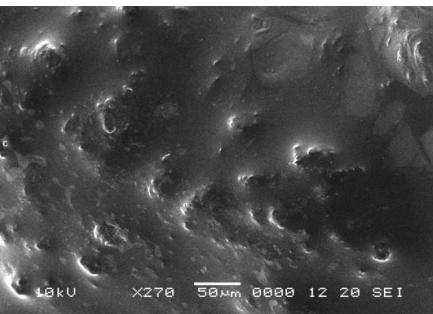
improve with increased levels of polyesteramide resin content. In addition, there was no evidence for the presence of rust (see Table 8 and Figure 3).



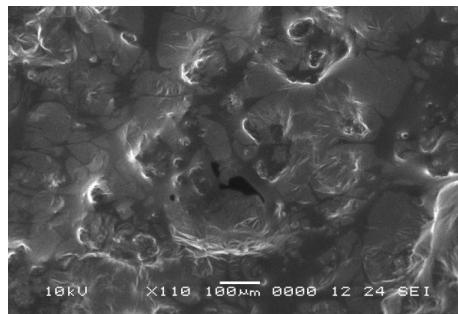
Asphalt cement not blended



Asphalt cement blended 6%PEA

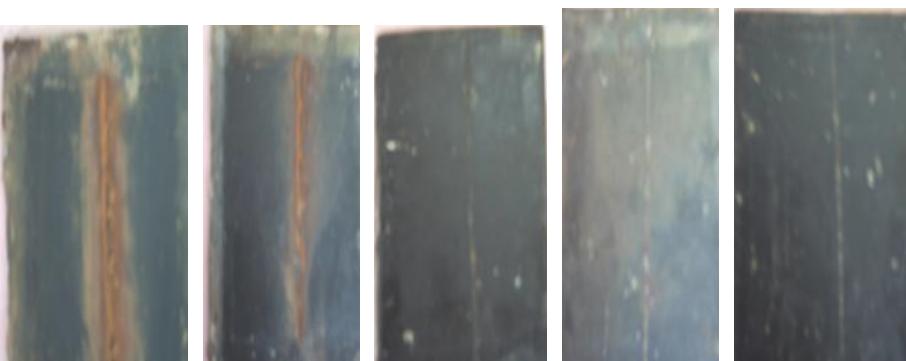


Asphalt cement blended 9%PEA



Asphalt cement blended 12%PEA

Fig.2 : The SEM micrographs of asphalt cement (first panels) and coating blend (next panels).



A B C D E

Fig 3: Corrosion resistance of coating blends**Table 5: Mixing ratio of asphalt cement with polyesteramide resin**

Resin NO.	Asphalt cement %	Polyesteramide resin %
A	100	-
B	97	03
C	94	06
D	91	09
E	88	12

Table 6: Physical characteristics of coating blends

Resin NO.	Colour (Gardner)	DFT (μm)	Air drying time(h)	Gloss at 60°	Adhesion	Scratch hardness (Kg)	Flexibility (Bend)
A	>18	80	24	55	5B	>5Kg	Poor
B	>18	80	24	88	5B	>2Kg	Pass
C	>18	87	9	60	5B	>2Kg	Pass
D	>18	92	7	65	5B	>2Kg	Pass
E	>18	95	7	78	5B	>2Kg	Pass

Table 7: Chemical resistance of coating blends per days

Resin NO.	Water resistance	Acid resistance	Alkali resistance	Solvent resistance
A	>90	84	21	2
B	>90	>90	40	2
C	>90	>90	>40	2
D	>90	>90	>70	2
E	>90	>90	>80	4

Table 8: Evaluating degree of blistering and rating failure at scribe of coating blends

Resin NO.	Blistering		Scribe failure (rating number)
	Size	Frequency	
A	2	Medium Dense	4
B	4	Medium Dense	5
C	6	Medium	6
D	8	Few	8
E	10	-	9

4. Conclusion

The data obtained from the study revealed that the blend of polyesteramide resin and asphalt cement was better blend coating properties. The coating blend was studied using SEM and the components present were found to be compatible. Chemical testing indicated that the coating blends offered good coating resistance when exposed to a salt-spray environment and mechanical testing indicated very good properties with respect to adhesion, flexibility, gloss and scratch hardness which attributed to the combination of thermosetting and thermoplastic resins. The asphalt cement blended into the resin, due to high resistance to moisture and good adhesion properties regarding to the steel substrate. The incorporation of polyesteramide resin improved the asphalt cement drying time, gloss, scratch hardness, chemical and corrosion resistance.

References

1. M. Yaseen and W. Fure, J. Oil Color Chem. Assoc., 61,284 (1978).
2. M. Gavrila, J.P. Millet, H. Mazille, D. Marchandise and J.M. Cuntz, electrodeposited on steel, Surface & Coatings Technology 123 (2000) 164–172.
3. M. Kraljic, Z. Mandic and Lj. Duic, Corrosion Science 45(2003) 181– 198.
4. N.M. Martyak, P. McAndrew, J.E. McCaskie and J. Dijon, Progress in Organic Coatings 45 (2002) 23–32.
5. A.M. Fenelon and C.B. Breslin, Synthetic Metals 144 (2004)125–131.
6. J.I. Martins, T.C. Reis, M. Bazzaoui, E.A. Bazzaoui and L. Martins, Corrosion Science 46 (2004)2361–2381.
7. J. E. O. Mayne and J. Mills, J. Oil Color Chem. Assoc., 58,155(1975).
8. J. F. McIntyre and H. Leidheiser Jr., J. Electrochem. Soc., 133, 43 (1986).

9. J. Parks and H. Leidheiser Jr., Ind. Eng. Chem., Prod. Res. Da., 25, 1 (1986).
10. H. Corti and R. Fernsndez-Prini, Prog. Org. Coat., 10, 5 (1982).
11. H.M. Park et al. Construction and Building Materials 23 (2009) 219– 225.
12. G.D. Airey et al. Fuel 87 (2008) 1763–1775.
13. M. C. Shukla, and A.K. Vasishtha, J. Oil Color Chem. Assoc.69, 3 (1986).
14. H.A. El-Wahab et al., Progress in Organic Coatings 66 (2009) 242– 247.
15. H.A. El-Wahab et al., Pigment and resin technology 40, issue5 (2011) 305-310.
16. ASTM Method: D 1640-95.
17. ASTM Method: D 523-89 (Reapproved 1994).
18. ASTM Method: D 3363-92a.
19. ASTM Method: D 1005-95.
20. ASTM Method: B 117-90.
21. ASTM Method: D 714-87 (Reapproved 1994).
22. ASTM Method: D 1654-92.
23. ASTM Method: D 610-95.
24. ASTM Method: D 3359-95a.
25. ASTM Method: D 522-93 a.
26. ASTM Method: D 609-95.
27. T. Learner, Analysis of Modern Paints, Getty Publication, Canada, 2004.
28. Z.W. Wicks Jr., F.N. Jones, S.P. Pappas, Organic Coatings: Science and Technology, Vol. 1: Film Formation, Components and Appearance, John Wiley & Sons, Inc., New York, 1992.