omplete Specification

The present invention relates to an anticorrosive coating composition with polyaniline useful for corrosion protection of steel reinforcement in concrete structures

The present invention also relates to a process for the preparation of an anticorrosive coating composition with polyaniline useful for corrosion protection of steel reinforcement in concrete structures

Background of the invention

Concrete structures such as bridges, buildings, elevated highways, tunnels, parking garages, offshore oil platforms, piers and dam walls are containing reinforcing steel The main cause of degradation of reinforced concrete structures is corrosion damage to the rebar embedded in concrete The two most common causes of reinforcement corrosion are (a) localized breakdown of passive film on the steel by chloride ions and (b) general breakdown of passivity by neutralization of the concrete, predominantly by reaction with atmospheric carbon di oxide

According to a 1997 report, of the 581,862 bridges in and off the USA federal aid systems, about 101,518 bridges were rated as structurally deficient The average annual cost, through year 2011, for just maintaining the overall bridge conditions, i e , the total number and the distribution of structurally and functionally deficient bridges, was estimated to be $5 2 billions The magnitude of this corrosion problem in the construction industry has increased significantly in the last three decades and is likely to keep increasing

Given the importance of the costs associated with the construction industry, it is essential to adopt all possible methods to controlling corrosion in concrete structures Use of good construction design and procedures, adequate concrete cover depth, corrosion inhibiting admixtures and low permeability concrete alone will not abate the corrosion problem, because concrete has a tendency to crack inordinately This situation essentially leaves the reinforcing steel itself as the line of defense against corrosion For this reason, use of a coating system on the reinforcing steel is even more critical in abating this costly corrosion problem Hitherto a number of coating systems such as zinc coating (galvanizing), fusion bonded epoxy coating, cement based coating and other polymer coatings have been used as protective coatings for reinforcement bars with advantages and limitations Zinc coating being a sacrificial coating that will give protection only for a limited period and thus will not eliminate the corrosion process, but will only postpone it {R N Swamy, "Corrosion of Reinforcement in Concrete Construction", (Ed C L Page, K W J Tradaway and P B Bamforth), Elsevier Applied Science, London, 1990, 586} Cement based coatings, even though cost effective, are laborious field process and have to be applied after bending operations {NS Rengaswamy, S Snnivasan and TM Balasubramanian, "Inhibited and Sealed Cement Slurry Coatings of Steel Rebar -A State of Art Report" Transactions of the SAEST, Vol 23, No 2-3, 163, 1988}

Fusion bonded epoxy coating provides only barrier protection and also affect bond strength to a considerable extent {H M Makhlouf, AAI-Tamini and AH Akbari, "Bond carrying capacity of epoxy coated reinforcement", Proceedings of International Conference on Corrosion and Corrosion Protection of Steel in Concrete, (Ed R N Swamy), Sheffield Academic Press, UK, 24-28, July, 1994, 1218-1230}

Hitherto it is reported that most of the organic coatings contain pin holes and accelerated corrosion of steel takes place through pin holes In order to prevent the corrosion of steel in pin holes, coating system containing conducting polymer such as polyaniline is highly useful The conducting polymer present in the coating system is able to passivate the pin holes and offers corrosion protection of steel

containing coating is able to protect steel in acid and
d J Posdorfer, Electrochimica Acta, 44 (1999) 2139, D
Thompson and C J Brya, Poly Chem 35(1994)265, TP
Mc Andrew, TRIP, 5 (1997) 7]

Hitherto it is shown that the coating containing polyaniline is able to protect the scratches and pin holes in the coating by repassivation of exposed areas [W K Lu, R L Elsenbaumer and B Wesshng, Synthetic Metals, 71 (1995) 2163, P J Kinlen, V Menon and Y Ding, J Electrochem Soc , 146 (1999) 3690, B Wesshng, Synth Metals, 85(1997)1313]

Hitherto no report is available on the usage of polyanihne containing coating for protection of steel in concrete

Objectives of the invention

The main objective of the present invention is to provide a self-passivating anticorrosive coating composition containing polyanihne as pigments useful for corrosion protection of steel in concrete

Another objective of the present invention is to provide a process for the preparation of an anticorrosive coating composition with polyanihne useful for corrosion protection of steel reinforcement in concrete structures

Summary of the invention

Accordingly the present invention provides an anticorrosive coating composition useful for corrosion protection of steel reinforcement in concrete structures comprising

b) epoxy resin in the range of 29-31 parts,

c) polyamide curing agent in the range of 8-9 parts,

d) titanium-di-oxide in the range of 4-5 parts,

e) polyanihne pigment in the range of 5-6 parts,

f) talc in the range of 2-3 parts,

g) silica in the range of 1-2 parts,

h) solvent in the range of 44-46 parts of total composition

In an embodiment of the present invention the solvent used is a solvent mixture of xylene, methyl isobutyl ketone (MIBK) and cellosolve

In yet another embodiment the anticorrosive coating composition the following characteristics

a) dry film thickness of the coating composition is 38 - 40 (j,m / coat,

b) volume solids is in the range of 33-35 %

c) pigment volume content (P V C) is in the range og 30-35 % ,

d) area coverage by coating composition is 10-11 sq m/ litre,

e) initial coating resistance of coated steel panel in cement extract after 1 day is in the range of 290-295 K   cm2,

f) final coating resistance of coated steel panel in cement extract after 90 days is in the range of 540-545 K   cm2,

g)) initial coating capacitance of coated steel panel in cement extract after 1 day is 1 80-1 90 nF cm-2, h) final coating capacitance of coated steel panel in cement extract after 90 days is 0 45-0 50 nF cm-2, The present invention further provides a process for the preparation of anticorrosive coating composition useful for corrosion protection of steel reinforcement in concrete structures comprising the steps of

a) preparing a homogenous binder solution by refluxing epoxy resin with a solvent mixture of xylene, methyl isobutyl ketone (MIBK) and cellosolve,

b) pre-mixing anatase titanium-di-oxide, passivating polyanihne pigment, silica, talc along with aluminium stearate using an attntier for a period of 30-60 minutes,

c) adding pre-mixed pigments obtained in step (b) to the binder solution obtained in step (a), followed by charging in a ball mill and running it for a period of 45-50 hrs,

mill, known as base and storing it in

... with an amine value of 280-320 KOH/g by mixing it with Xylene MIBK solvent mixture and separately stored in an air tight container,

f) mixing the base obtained in step (d) with hardener obtained in step (e) ratio of 3 1 to 3 12, followed by stirring for a period of 15-20 mm to obtained the desired coating composition

In still another embodiment the coating composition obtained is useful for corrosion protection of steel reinforcement in concrete structures

Detail description of the invnetion

The process involves the preparation of polyaniline pigment and an anticorrosive coating system with polyaniline The polyaniline was prepared using the following ingredients Aniline 0 9 to 1 1 M Hydrochloric acid 0 9 to 1 1 M Ammonium persulfate 0 9 to 1 1 M Water 500-700 ml pH 1 to 2 Temperature $5 \pm 1 \, ^\circ$ C

The anticorrosive coating system containing polyaniline was prepared using the following ingredients

(Table Removed)

The properties of the anticorrosive coating are as follows

Dry film thickness 38 - 40 µm / coat

Volume solids 35 %

Pigment Volume Content (P V C) = 35 %

Area coverage 10 - 11 sq m / litre

The following examples are given by way of illustration of the working of the invention in actual practice and should not be construed to limit the scope of the present invention

Example I Complete immersion Test

Under this example, the performance of anticorrosive coating system with polyanihne on steel exposed in simulated concrete environment (pH=12 2) has been found by immersing the coated sample in cement extract for a period of 90 days and visually inspected Preparation of Polyanihne pigment

1M of distilled aniline was dissolved in 500 ml of 1M HCI Pre-cooled 1M solution of ammonium persulfate was added drop wise to the pre-cooled aniline-acid mixture for about 1 5 hours with constant stirring The reaction was conducted at $5 \pm 1 \, ^\circ$ C After the addition, the stirring was continued for 2 hours for ensuring complete polymerization A dark green coloured conducting polyanihne thus formed was filtered and repeatedly washed with distilled water to remove the excess acid content The polymer was air dried for 1-2 hours and oven dried at about 80° C for 2 hours The dried polyanihne was fine grinded using mortor and pestle and then used as pigment .

Preparation of coating system containing polvaniline

170 gms of epoxy resin of epoxy equivalent 480 - 500 is refluxed with 170 c c of Xylene, MIBK, Cellosolve solvent mixture to get a homogenous binder solution Anatase titanium-di-oxide (246 gms), passivating polyanihne pigment (74 gms), silica (61 gms), talc (89 gms) are pre-mixed along with aluminium stearate (21 gms) These pre-mixed pigments are slowly added to the binder solution and charged in a ball mill The ball mill is run for 48 hours or it is run till the coating gets a hegmann gauge value of 8 - 9 The coating is then removed from the ball mill If attntor is used then it is run for 60 minutes The coating is stored in an air tight container (Base) 62 gms of polyamme hardener (Amine value 280 - 320 mg KOH/gm) is mixed with 62 c c of xylene MIBK solvent mixture and stored in an air tight container separately (Hardener)

3 parts of base is mixed with 1 part of the hardener and the coating is stirred well for 15 minutes before application.

...ortland pozzolana cement At first, 100 grams of Portland ...00 cc of distilled water in a Microid flask shaker for one hour The cement extract was then filtered through No 1 Wattman filter paper This cement extract simulates the concrete environment

The mild steel panels of size 7 5 cm X 5 cm X 0 2 cm was coated with the anticorrosive coating with polyaniline by brush after sand blasting to SA 2 5 The coating was allowed to dry for a period of 48 hours After drying, the coated samples were completely immersed in cement extract for a period of 90 days At the end of the test period, the coated samples were visually inspected The test results are given in Table -1

Table-1 Results of Total Immersion studies

(Table Removed)

From the above result, it is observed that the anticorrosive coating containing polyaniline has performed well in simulated concrete environment even after 90 days of exposure

Example -21 Potential measurements

Under this example, the corrosion resistance of anticorrosive coating containing polyaniline has been examined by measuring the potential of the coated panel exposed in cement extract The coated sample was prepared as described in Example - 1 A glass tube of 1 cm diameter and 3 cm height was fixed on the coated sample using adhesive (M-seal) Then, the glass tube was filled with cement extract and a saturated calomel electrode (SCE) was placed inside the cement extract The potential of the steel sample was measured by making electrical contact with the

painted panel using high impedance volt meter The results obtained are given in Table - 2

Table-2 Results of Potential measurements

(Table Removed)

It can be seen from the test results that the high negative value of potential after 24 hours of immersion indicates the onset of corrosion at pinholes of the coating system With time proceeds, the potential has shifted towards noble direction indicating the repassivation of base metal exposed in pinholes The high positive values even after 90 days of immersion in cement extract is an indication of higher protective ability of the coating The high positive potential value is due to the formation of passive film on steel substrate by polyaniline pigment

Example 3 Impedance Measurements

Under this example, the corrosion resistance of anticorrosive coating containing polyaniline has been found out by impedance measurements on coated panel in cement extract The coated mild steel panel as described in Example II, was tested by impedance method by using EG&G Electrochemical impedance analyzer (Model 6310) The results obtained are given in Table 3

Table-3 Results of Impedance measurements

(Table Removed)

The above results clearly show that the coating resistance increases with time due to repassivation of base metal at pinholes, which substantiates the observation in Example II The higher coating resistance and lower capacitance of coated steel even after 90 days of exposure indicate the high corrosion resistance property of the coating system

Example - 4 Applied Voltage Test

Under this example, the resistance of anticorrosive coating with polyaniline against chloride permeation has been tested by applied voltage test as per ASTM A 775/A 775M - 90

diameter and 100mm length were taken The rebars were coated with polyaniline system as described in Example 1

After the curing period, one end of the rebar was soldered with insulated copper electrical wire to serve as electrical contact point The other end of the rebar was protected with an insulating material to a length of 25 mm The coated rebars were suspended vertically in a transparent non conductive plastic container of size 150 x 150 x 900 mm The container was filled with an aqueous solution of 7% NaCI to a height of 800mm The coated rebars were suspended vertically so as to have a clearance of 25mm from the bottom, 40mm from each sides and 40mm in between the rebars The exposed area of the rebar on which the test conducted was 240 cm2

In this test, one rebar act as anode and the other rebar act as cathode A potential of 2V was impressed between the coated rebars for a period of 60 minutes using a DC regulated power supply unit (Aplab L3220S) The voltage between the coated rods was measured by a high impedance voltmeter The current was measured for every 5 minutes intervals using an Avometer After the test was over, the surface condition of the rebar, which acts as anode, was visually examined for any corrosion products of iron The other rebar, which acts as cathode, was also visually examined for any coating failure due to evolution of hydrogen

Table 4 Results on applied voltage test (after 60 minutes)

(Table Removed)

From the experimental results, it can be seen that the anticorrosive coating with polyaniline coated rebar has shown zero current throughout the test period indicating its resistive ability against the penetration of chloride ions The visual observation also reveals that there is no hydrogen evolution and coating disbondment on the rebar surface which acts as cathode No rust products were observed on the other rebar surface, which acts as anode This result clearly indicates the perfect protective nature of the anticorrosive coating system with polyaniline even in the presence of 7% chloride

Example - 5 Time to cracking study

Under this example, the corrosion resistance of the anticorrosive coated rebars embedded in concrete has been studied by an accelerated time to cracking study as perASTMC1202 Cylindrical concrete specimens of size 50 x 150 mm with a design strength of 20 MPa have been cast for this study 10mm diameter and 150mm length mild steel rebar coated with anticorrosive coating with polyaniline was used as reinforcement bar The surface preparation of rebar and application of anticorrosive coating with polyaniline on the rebars was done as described in Example 1

After curing period was over, one end of the rebar was soldered with insulated copper electrical wire to serve as electrical contact point The other end of the rebar was protected with an insulating material to a length of 25 mm This coated rebar was centrally positioned in the concrete during casting and kept in potable water for 7 days Afterwards, the reinforced concrete specimen was kept in a glass container of size 160 x 200mm A cylindrical perforated stainless steel auxiliary electrode of area 600 cm2 was also kept in the glass container and then it was filled to a height of 150mm with an aqueous solution of 3 5% NaCI

In this test, the embedded coated specimen acts as anode and the external stainless steel cylindrical electrode serves as cathode A constant potential of 6V was applied between the embedded rebar and stainless steel electrode using a DC power supply unit (Aplab L3220S) Then, by using an Avometer, the variation of current with time was measured for every 12 hours An increase in current indicates the on set of corrosion and cracking of the concrete is visible there after During the test period, the reinforced concrete specimens were visually

every 24 hours When cracking was noticed on the
were removed from the container for broken open of
was visually examined for the appearance of rust
products The results obtained on this test are presented in Table 5

Table 5 Results on time to cracking study

(Table Removed)

From the experimental results, it can be seen that the concrete specimen embedded with anticorrosive-coated rebar cracks only after 720 hrs of exposure The visual observation also reveals that only very few rust products appeared only at selected portions of the anticorrosive-coated rebar

Example - 6 Anodic polarization studies

Under this example, the corrosion resistance of the anticorrosive coating with polyanihne pigment has been tested by anodic polarization of rebar coated with anticorrosive coating in aqueous cement extract with 1000 ppm of chloride

Mild steel test specimen of size 12mm diameter and 25mm height was coated with anticorrosive coating with polyaniline was immersed in aqueous cement extract containing 1000 ppm of chloride The anticorrosive coating was applied on the rebar as per the procedure described in Example 1

The test specimen coated with anticorrosive coating was anodically polarized by applying a current density of 290 µA/crn2 using stainless steel electrode as cathode The variation in potential with time was measured with reference to saturated calomel electrode (SCE) This variation in potential was monitored for fifteen minutes using SI 1280 electrochemical system (Solartron UK) The results obtained on anticorrosive coated rebar is given in Table 6

Table 6 Results on anodic polarization studies

(Table Removed)

From the experimental results, it can be seen that the potential of coated rebar has raised above the oxygen evolution potential and it has remained almost steady throughout the test period at that potential This clearly indicates the high impermeable and high resistive behaviour of anticorrosive coating system against chloride attack

The visual observations on the coated specimens also reveals that no rust spot or failure of coating system was observed on the anticorrosive coated rebar even in presence of 1000 ppm of chloride present in cement extract

The main advantages of the present invention are

(i) The anticorrosive coating system containing polyaniline offers higher corrosion protection of steel in concrete (ii) The anticorrosive coating system containing polyaniline is able to repassivate the steel at pin holes and arrests the corrosion of steel in pin holes (iii) The anticorrosive coating system containing polyaniline performed well in simulated concrete environment (pH=12 2) even after 90 days of exposure (iv) The potential studies reveals that the anticorrosive coating system containing polyaniline offers repassivation of base mental at pinholes even after 90 days of exposure in simulated concrete environment (v) The impedance studies reveal that the anticorrosive coating with polyaniline shows higher charge transfer resistance and lower capacitance values even after 90 days of exposure in cement extract (vi) The anticorrosive coating with polyaniline is able to resist the chloride permeation even in presence of 7% NaCI in an aggressive test known as applied voltage technique (vn) The anticorrosive coating with polyaniline is able to withstand

te reinforced with the anticorrosive
NaCI in an aggressive test known as
time to cracking study (VIII) The anticorrosive coating with polyaniline is able to tolerate 1000 ppm of
chloride in a highly aggressive test known as anodic polarization technique (ix) The coating system containing polyaniline is able to replace the
conventional toxic pigment based coatings.

We claim:

1 An anticorrosive coating composition useful for corrosion protection of steel reinforcement in concrete structures comprising:

a) epoxy resin in the range of 29-31 parts
b) polyamide curing agent in the range of 8-9 parts,
c) titanium-di-oxide in the range of 4-5 parts,
d) polyaniline pigment in the range of 5-6 parts,
e) talc in the range of 2-3 parts,
f) silica in the range of 1-2 parts,
g) solvent in the range of 44-46 parts of total composition

2.An anticorrosive coating composition as claimed in claim 1, wherein the solvent used is a solvent mixture of xylene, methyl isobutyl ketone (MIBK) and cellosolve.

3.An anticorrosive coating composition as claimed in claim 1 has the following characteristics:

a) dry film thickness of the coating composition is 38 - 40 µm/ coat,
b) volume solids is in the range of 33-35 %
c) pigment volume content (P.V.C) is in the range og 30-35 % ,
d) area coverage by coating composition is 10 - 11 sq. m / litre,
e) initial coating resistance of coated steel panel in cement extract after 1 day is in the range of 290-295 K   .cm2,
f) final coating resistance of coated steel panel in cement extract after 90
days is in the range of 540-545 K   .cm2,
g)) initial coating capacitance of coated steel panel in cement extract after
1 day is 1.80-1.90 nF. cm-2, h) final coating capacitance of coated steel panel in cement extract after 90 days is 0.45-0.50 nF.cm-2, 4. A process for the preparation of anticorrosive coating composition useful for corrosion protection of steel reinforcement in concrete structures comprising the steps of:

a) preparing a homogenous binder solution by refluxing epoxy resin with a solvent mixture of xylene, methyl isobutyl ketone (MIBK) and cellosolve,
b) pre-mixing anatase titanium-di-oxide, passivating polyaniline pigment, silica, talc along with aluminium stearate using an attritier for a period of 30-60 minutes,
c) adding pre-mixed pigments obtained in step (b) to the binder solution obtained in step (a), followed by charging in a ball mill and running it for a period of 45-50 hrs,
d) removing the coating from the ball mill, known as base and storing it in an air tight container,

ith an amine value of 280-

MIBK solvent mixture and

ner,

f) mixing the base obtained in step (d) with hardener obtained in step (e) ratio of 3:1 to 3: 1.2, followed by stirring for a period of 15-20 min to obtained the desired coating composition.