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Steel protective coatings of cottonseed oil alkyd modified urethane/mercapto methyl tetrazole adduct

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ABSTRACT

The growing interest toward energy conservation and green environment driven the coating technologists to replace petroleum based polymeric binders with renewable sources. Cottonseed oil alkyd (CSA) was prepared in the laboratory by alcoholysis of cottonseed oil with glycerol followed by esterification with phthalic anhydride and an excess of pentaerythritol to obtain the polymer with excess hydroxyl value. The structure of CSA polymer was confirmed by FTIR spectral analysis and its molecular weight was investigated by gel permeation chromatography (GPC). Instantly before coating steel surface, CSA was modified by reaction with TDI at room temperature to introduce polyurethane linkage and got modified cottonseed alkyd modified urethane (CSAU) coat. Thermo gravimetric analysis (TGA) was used to investigate the thermal stability and curing behavior of the modified CSAU coating. The modified CSAU paints were formulated and prepared. The performance of high molecular weight heterocyclic 5-mercapto-1-methyl tetrazole adduct (MMT) in the modified paint (CSAU/MMT) was studied. Drying time tests, crosscut adhesion test, impact strength, pencil hardness, chemical and water resistance were used to evaluate the modified CSAU and CSAU/MMT paints. Corrosion resistance tests, including blistering, scribing and unscribing area of metal surface in 5% NaCl solution in addition to the weight loss determination of steel are specialized corrosion tests to evaluate CSAU and CSAU/MMT as anticorrosive paints. It was found that cottonseed oil could be modified successfully and replace petroleum raw materials in anticorrosive coatings and paint industries. It exhibited good physical, mechanical performances and chemical resistance. It's characterized by high thermal stability. Incorporation of only 0.02% MMT adduct to CSAU paint, increased the corrosion inhibition efficiency to a higher extent.

KEYWORDS

Cottonseed oil;
Alkyd;
Paint;
Corrosion inhibitor.

INTRODUCTION

Vegetable oils are renewable source compounds which commonly used in producing valuable polymeric materials such as epoxy, polyesteramide, alkyd and polyurethane. In addition to its many applications in other areas vegetable oils commonly used in the composition of paints and varnishes[1-4]

According to iodine value (which is a measure of unsaturation present), the oils can be classified to drying oils (iodine value > 140), semidrying (iodine value 125- 140), nondrying oils (iodine value < 125)[5].

Cottonseed oil has a 2:1 ratio of polyunsaturated to saturated fatty acids. Its fatty acid profile generally consists of 70% unsaturated fatty acids, including 18% monounsaturated (oleic) and 52% polyunsaturated (linoleic) and 26% saturated (primarily palmitic and stearic)[6]. Iodine value of cottonseed oil is 103-116, so it can be classified as nondrying oil[5].

Alkyd resins are used for decorative painting applications more than other binders because of lower cost; low price of alkyd resins related to inexpensive raw material, easy manufacturing and high solubility of resin in less expensive solvents. Alkyd resins not only are used in decorative paints, but also mainly are applied in air drying and stoving paints, inks, machine toll finishes and clear, matt and semi matt varnishes of wood furniture[7].

Polyurethanes on the other hand, exhibit faster drying time, better abrasion resistance, toughness, chemical and UV resistance when compared to alkyd resins. Extensive applications of polyurethane can be found in high performance coatings, such as that of automotive applications and wood industries. The presence of urethane linkage enhances properties of alkyd resins in terms of morphology, viscosity, adhesion, hardness and impact strength over individual resins[7-12].

High molecular weight Heterocyclic corrosion inhibitors, especially those containing both sulfur and nitrogen, play an important role in the protection of steel. These compounds can be adsorbed on the metal surface through the lone pair of electrons present on heteroatoms in addition to active terminal groups in the basic polymer structure[13-18]. They can replace inorganic anticorrosive pigments. They are colorless and accept any decorative pigments in the paint formulations. They have wide applications in anticorrosive paints rather than other applications like in protection of steel alloys in oil fields[18-20].

The present work investigated the synthesis of cottonseed oil alkyd with the excess hydroxyl group (CSA). Its modification with TDI and preparation of cottonseed oil alkyd modified urethane (CSAU) paints was done and applied in the field of anti-corrosion of steel. Performance of high molecular weight heterocyclic 5-mercapto-1-methyl tetrazole (MMT) adduct as corrosion inhibitors in the CSAU paints was studied. Thermal behavior of the modified coating was studied using TGA technique. Physical, mechanical and chemical resistance properties of all paint formulations were studied. Corrosion tests in addition to weight loss technique were used to evaluate the modified paints in the absence and presence of MMT adduct for protection of steel.

MATERIALS

Cottonseed oil is, iodine value 103- 116, delivered from John L Seaton & Co Ltd, England. Pentaerytritol is delivered from Perstorp Company, USA. Phetalic anhydride is delivered from IG. Petrochemical Company of India, melting point 133 °C and acid number 391 mg KOH/g fatty acid, maleic anhydride from USP Technology Group of Taiwan, melting point 54 °C and acid number 522 mg KOH/g fatty acid, Glycerol from EVYAP Company from Turkey, purity percent 99.5%, Pentaerythritol from Koninda, Canada, melting point 248 °C. Toluene diisocanate TDI is delivered from Lyondell Chemical Company, USA. Titanium dioxide (Rutile R-902) has a density of 4.1 g/cm^3 and oil absorption 18.8 g/ 100g, and is a product of Du-Pont Company, Canada. Talc powder s delivered from Global Misr Co., Egypt.

EXPERIMENTAL

Preparation of cottonseed oil alkyd resin

Cottonseed oil alkyd resin was prepared in two stages. The first stage was the alcoholysis stage at which monoglyceride was first prepared by reacting calculating quantities of cottonseed oil with glycerol. The cottonseed oil was heated to 230 ± 5°C with high agitation speed and N2 sparging. Glycerol and 0.05% Litharge catalyst per each 100g of the oil.

The second stage was esterification of monoglyceride mixture with phthalic anhydride. The temperature was maintained in the range of 230 ± 5°C. Then excess quantities of pentaerythritol were added in order to increase the hydroxyl value.

Characterization of the prepared cottonseed oil alkyd

Acid value is made by titration of the sample with standardized potassium or sodium hydroxide solution according ASTM D 1639-90.

According to ASTM D 1957- 01, Hydroxyl number is defined as the milligrams of KOH equivalent to the gram of the substance (resin) taken. It is used to find out the amount of curative (TDI) required for the formulation.

Hydroxyl number = (B-V) × N×56.1/S×10

Where, B is the volume of NaOH consumed by the blank.V is the volume of NaOH consumed by the sample in ml. N is the normality of NaOH. S is the weight of sample in grams.

The prepared cottonseed alkyd resin (CSA) is standardized by FTIR[21,22]. The chemical compositions of alkyd resin are recorded by JASCO FT/IR 6100 in the range of 4000–400 cm^{-1}.

Gel permeation chromatography technique not only have used for determination of the distribution of molecular weight of resins which is called polydispersity (PDI), but also have applied for determination of numeric average molecular weight (Mn), weight average molecular weight (Mw) Weight-average (Mw), number-average (Mn). The used instrument is Agilent 1100 series (GPC), Germany, equipped with G1362A refractive index detector with 100-104-105 A° ultrastyragel columns. Polystyrene was used as a standard. N,N-dimethylformamide (DMF) was used as an eluent with a flow rate of 1 ml min^{-1}.

Modification of CSA and CSAU paint formulations

CSA was blended with TiO_2 pigment, dispersing and anti-skinning agent in the miller paint for more than 2 hours. Immediately and before application on the steel surface, a calculated amount of TDI (according to the hydroxyl number) was divided and added stepwisely each 20 minutes to prevent gelation of the coat as a result of the sudden addition of TDI.

Evaluation of the prepared modified paints

Both Steel and glass panels were cleaned by mixture of pure solvents according to ASTM D2201-06, and ASTM D3891-08, respectively.

The wet paint was applied to steel and glass panels with different thicknesses (60, 90, 100, 200 μm) using film applicator according to ASTM D823-07.

A variety of physical, mechanical, chemical resistance and corrosion inhibition evaluations of the paint films were carried out according to relevant methods and after drying of films for 7 days.

Pencil hardness was done with an Erichsen scratch hardness test kit according to ASTM D3363-05 under room temperature conditions and the hardest pencil grade from soft to hard (6B to 6H) that did not rupture or scratch the coating was termed the pencil hardness of the test specimens.

Bending test of a dry paint film was determined over cylindrical mandrels of 6mm diameters according to ASTM D522-08.

Adhesion test is done according to ASTM D3359-09.

Water resistance of paint films was done by dipping them in water for 24 hours according to ASTM D1647-89.

The chemical resistance of paint films was determined on coated glass plates. The plates were immersed in alkali solution (5% NaOH), acid solution (5%HCl), hydrocarbon solvent (xylene) and polar solvent (acetone) for 48 hours.

Degree of Blistering of Paints is evaluated according to ASTM D 714-09.

Evaluation of scribed and unscribed areas of painted steel panels in corrosive media of 5% NaCl up to 28 days are done according to ASTM 1654-08, and photos are picked up at the end time of the test.

Weight loss measurements of coated steel panels are subjected to the corrosive environment for more than 60 days, according to ASTM D 2688-05.

RESULTS AND DISCUSSION

Preparation and evaluation of CSA

TABLE 1 summarizes the composition and characterization of the prepared CSA.

Gel permeation chromatography (GPC)

GPC results of the of the prepared CSA are Mn= 2043 g/mol, Mw= 11021 g/mol, PDI= 5.39.

Where, Distribution of molecular weight of resins is called polydispersity (PDI), while average molecular

TABLE 1 : Composition and properties of cottonseed oil alkyd resin (A1)

Materials	Weight (*W*)	Equivalent weight	e_o	e_A	e_B	Functionality (F)	m_o
Cottonseed oil	172.814	293.0	0.58980	0.58980	0.58980	1	0.58980
Glycerol	23.746	31	0.77348		0.77348	3	0.25782
Pentaerythritol	67.8975	34.0	1.99698		1.996985	4	0.49924
Phehtalic Anhydride	114.044	74.0	1.54113	1.54113		2	0.77056
Maleic anhydride	0.518	49.0	0.01057	0.01057		2	0.00528

Excess OH = 56.911percent, acid number = 8 mg KOH/g, hydroxyl number = 195.295 mg KOH/g, produced water= 13.965
Notes: $k = (m_o / e_A)$, $R = (e_B / e_A)$, where: m_o - total moles present at start of reaction; e_A - number of acid equivalent; e_B - number of hydroxyl equivalents; e_o - total equivalents at start of reaction.
The above break-down is based on methods of calculation from alkyd resin technology, Patton, 1962[23].

weight (Mn) and weight average molecular weight (Mw).

FTIR spectroscopy

The IR spectra of the cottonseed oil alkyd resin is shown in Figure 1. In the IR spectrum. The broad band with high intensity at 3479 cm-1 corresponds to the hydroxyl group (-OH). A characteristic band at 1732 cm-1 is corresponding to aromatic (C=C) ring ester which, confirms the esterification of cottonseed oil monoglyceride with phthalic anhydride. The presence of O=C-O-C also exhibit characteristic ester band 1128 cm-1.

Cottonseed alkyd modified urethane coatings

Modification of CSA with urethane linkage is based on addition of toluene diisocyanate (TDI) step wisely to the excess hydroxyl CSA with a ratio of 1:10. Film formation is based on forming a crosslinking reaction between components, mixed immediately before application on the steel.

Thermo gravimetric analysis (TGA)

Thermal analysis of the cottonseed alkyd modified urethane (CSAU) sample was studied and plotted in Figure 2, The weight loss from room temperature (25°C ±2) to the onset decomposition temperature at 210°C is attributed to the removal of humidity and some volatiles present in the samples. The decomposition of the CSAU was gradual and consisted of three dominant steps. The first degradation step at 210°C was associated to the polymer chain scission and fatty acid aliphatic chain degradation in CSAU sample. Second degradation at 340°C related to the decomposition of urethane linkages, while third degradation step at 448°C

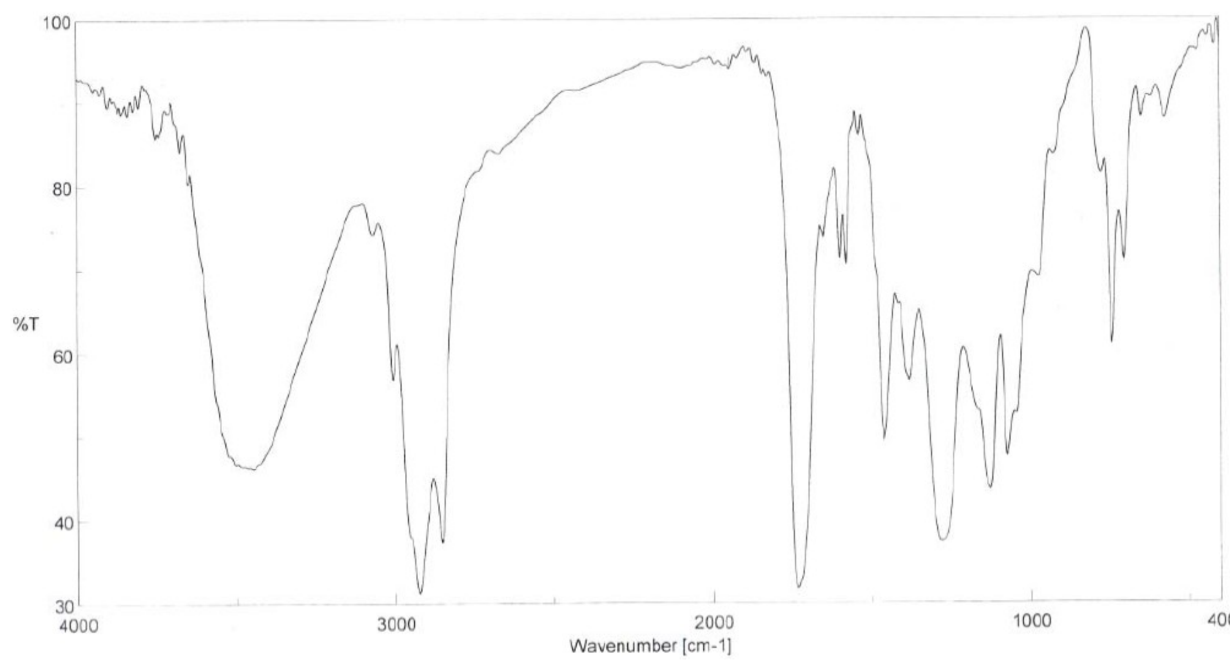

Figure 1 : FTIR spectra of the cottonseed alkyd polymer

corresponded to the aromatic moieties and ester group of the alkyd component.

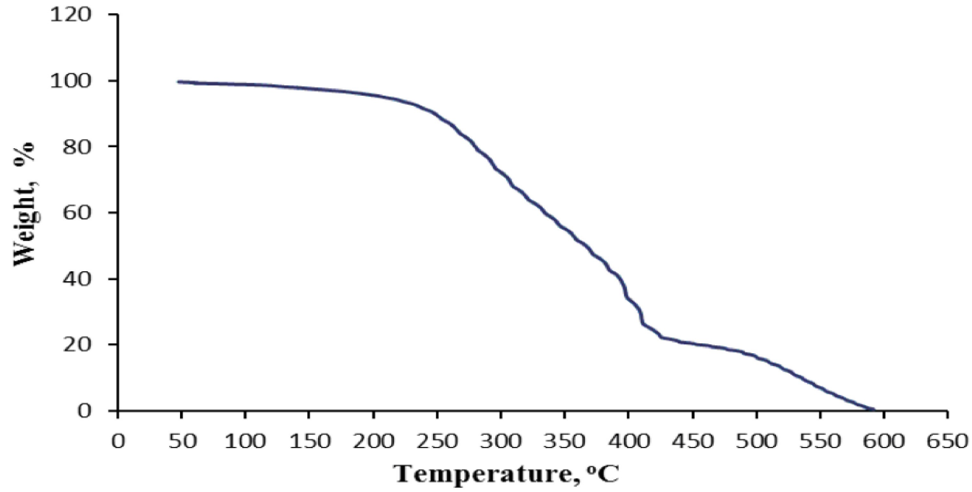

Figure 2 : TGA curve of CSAU coating

Preparation of cottonseed alkyd modified urethane paint formulations

As shown in TABLE 2, paint formulations of CSAU are prepared by blending 32g CSA (solid content 70%), 25.9g titanium dioxide as neutral pigment, 38.3g talc as a suitable filler for metal application, 0.5g dispersing agent in addition to antiskining agent with minimum amount of toluene solvent in the paint miller for 2hours. Immediately and before application on the steel surface, a calculated amount of 3.2g TDI (according to the hydroxyl number) was added stepwisely each 20 minutes to prevent gelation of the coat as a result of the sudden addition of TDI.

TABLE 2 : Paint formulations

Materials	Formula	
	Group1	Group2
	CSAU paint formula	CSAU/MMT paint formula
CSA	32.0	32.0
TDI	3.2	3.2
TiO_2	25.9	25.9
Talc	38.3	38.3
Dispersing agent	0.5	0.5
`Antiskining agent	0.1	0.08
MMT	-	0.02

Two groups of paint formulations were prepared. Group1: CASU paint formulation was prepared and applied to substrate with four different thicknesses (60, 90, 120 and 200μm). Group2: the prepared MMT adduct was prepared[24] and added to paint formula (CSAU/ MMT) with a very small concentration, 0.02% to study the performance of MMT as corrosion inhibitor and enhance the protection of steel.

Evaluation of the prepared CSAU paint formulations

The obtained results of physical, mechanical in addition to chemical and corrosion resistance tests were listed in TABLE 3. After 28 days of steel panels immersion in 5% NaCl, photos of the scribed coated area were picked up as shown in Figure 3

As shown in TABLE 3, the drying time (touch dry) was within 90 to 120 min. and the drying time increases with increasing the film thickness. All paint formulations exhibit good adhesion properties due to the inherent chemical structure of CSAU and its flexibility. The CSAUs paints also possessed comparatively good impact resistance and hardness. This can be attributed to the presence of urethane linkage and the ester linkage in the chains of polymers that provided flexibility while the aromatic composition of the polymer gave the hardness property[7]. It was also observed that as the thickness of the film increased, the impact resistance also increased. Good hardness of the film generally related to high extent of crosslinking[7,25].

According to the obtained results of chemical resistance tests, It was observed that the coated films were affected Small wrinkles in the NaOH resistance test arising from soft parts of the polymer with lower

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TABLE 3 : Physical & mechanical properties and corrosion test results of the prepared paint formulations

Test		Paint formula				
		CSAU paints				CSAU/MMT paint
		60 µm	90 µm	120 µm	200 µm	90 µm
Physical and mechanical test	Drying time, touch dry, min	90	100	120	120	120
	Adhesion test	4B	5B	5B	5B	5B
	Bending test, 6mm	pass				
	Impact resistance Kg/m	0.8	0.9	1.3	1.5	1.5
	Pencil hardness	-	-		B	B
Chemical resistance test, 48 h	5% HCl	Films unaffected				
	5%NaOH	Films small wrinkles				
	H_2O	Films unaffected				
	Xylene	Films unaffected				
	Acetone	Films slightly removed				
Corrosion test	Degree of blistering	-	4F	-	-	6F
	Rate of unscribed area	-	5	-	-	6
	Rate of scribed area	-	7	-	-	9
	Corrosion photos	Figure 3: Photos of scribed area of coated steel panels after 28 days immersion in 5% NaCl				

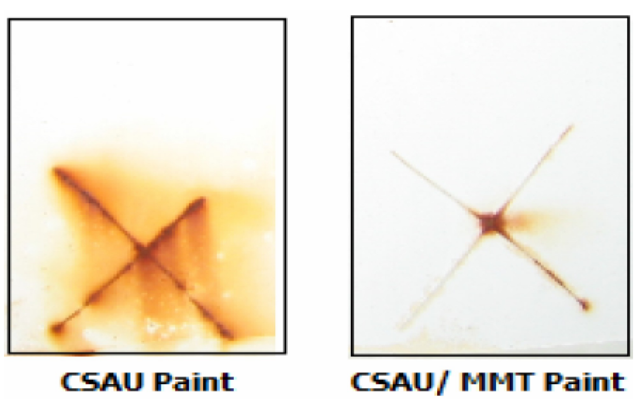

Figure 3 : Photos of scribed area of coated steel panels after 28 days immersion in 5% NaCl

crosslinking density. CSAU paint films unaffected by the acidic solution thus ensure high coating durability. The coated films unaffected in non-polar solvent such as xylene however, poor resistance in polar solvent (acetone) was detected and the films were slightly removed.

According to the corrosion inhibition efficiency results in TABLE 3, few blisters were detected films of both Group1 and Group 2 formulations corresponding to CSAU and CSAU/ MMT, respectively, but the difference in the size of blisters was smaller in case of CSAU/MMT due to extra adherence of the film to the steel by MMT adsorption. Less than 10% rust of unscribed area with negligible corrosion around the scribe was detected for CSAU/MMT coated steel panels. While 20% rust in the steel area under the CSAU paint films, in addition to moderate corrosion around the scribe were detected.

The obtained results go hand in hand with the picked photos of the coated steel panels at the end of corrosion resistance test, Figure 3.

Weight loss results of coated steel panels with CSAU paint (Group1) and CSAU/MMT paint (Group 2) formulations was plotted in Figure 4.

It is clear that, weight loss values of steel panels coated with CSAU paint were small and increased gradually with time. The modification of CSA with TDI exhibit the advantage of high intensity of crosslinking reactions, consequently drying of cottonseed oil with a low iodine value (103-116).

As a result of addition MMT adduct in CSAU/ MMT paint (Group2) formulation, lower weight loss was detected compared with Group I. A schematic representation of corrosion inhibition of steel in the presence of 0.02% MMT adduct is given in Figure 5. At this concentration, the adduct molecules may direct themselves to be adsorbed on the steel surface via the lone pairs of electrons on the sulfur atom of the (-SH) group and the oxygen atom of the hydroxyl group rather than the planarity of the heterocyclic structure, which is

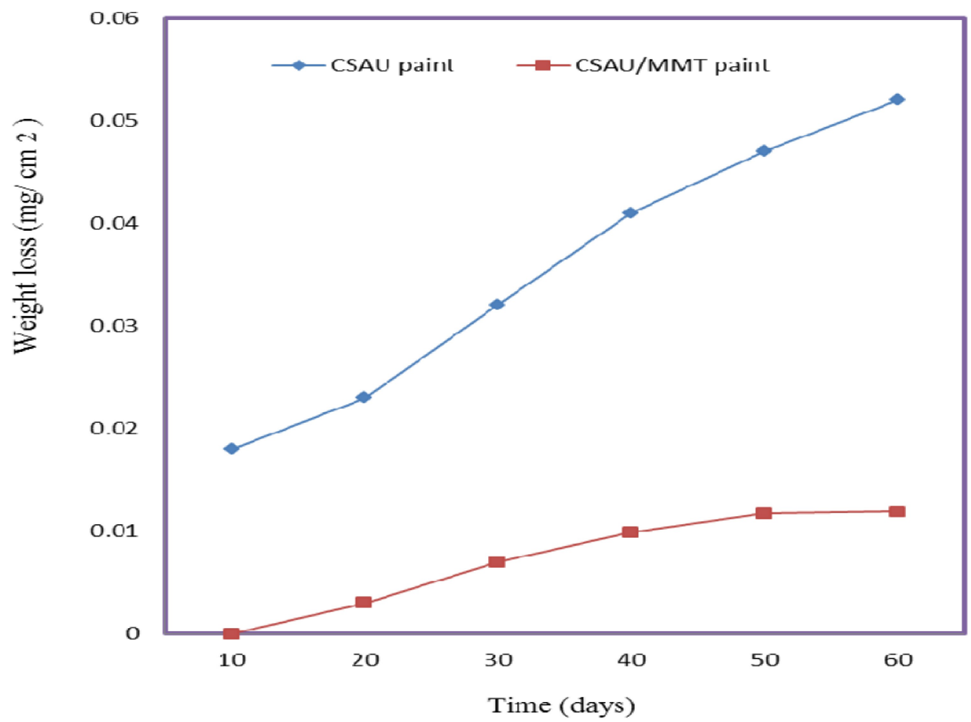

Figure 4 : Weight loss of coated steel panels with CSAU and CSAU/MMT paints

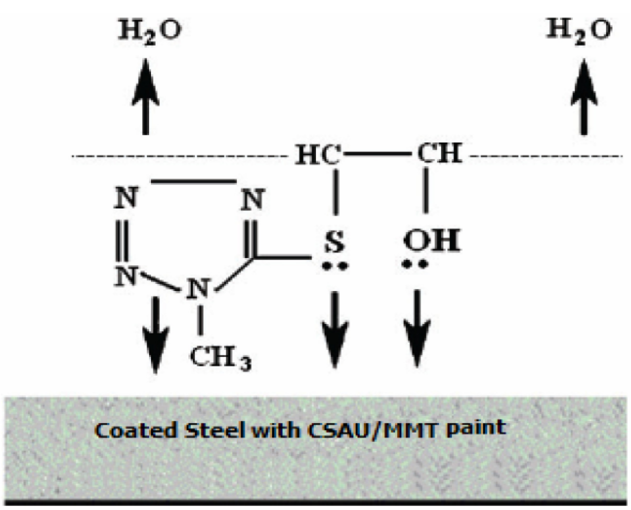

Figure 5 : Adsorption of MMT adduct on steel surface

rich with nitrogen atoms with high electron density, consequently the adhesion and protection of the paint films may be improved.

CONCLUSION

The renewable source, cottonseed oil could be modified successfully and replace petroleum raw materials in anticorrosive coatings and paint industries. It exhibited good physical, mechanical performances and chemical resistance. It's characterized by high thermal stability. The prepared MMT adduct increased the corrosion inhibition efficiency of the modified cottonseed oil paint with a very small concentration and without change in other measured properties.

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