CHAPTER IV
RESULTS AND DISCUSSION

Results and Discussion

The present experimental work is divided into two parts	
Part 1 **Preparation and Emulsification of some sulfur adducts**	
Part 2 **The emulsified adducts as corrosion inhibitors**	
Group I	*Optimization of pigment binder ratio for different emulsion paint formulations free of anti-corrosive pigments.*
Group II	*Optimizations of concentration of 2-mercapto-Δ^2-thiazoline adduct as corrosion inhibitor in water-borne urabrid AC100 paint formulations.*
Group III	*Evaluation and optimization of the best sulfur adduct as corrosion inhibitor in water-borne urabrid AC100 paint formulations for corrosion protection of mild steel.*
Group IV	*Evaluation of different binder systems (such as urabrid AC100, acrylic and short oil alkyd emulsion binder) containing the best prepared sulfur adduct.*
Group V	*A comparative study on the protective properties of emulsion paint formulations including the best sulfur adduct with those containing different anti-corrosive pigments.*

Results and Discussion

The corrosion of metals is a fundamental academic and industrial concern that has received a considerable amount of attention. Most of the well-known inhibitors are organic compounds containing heteroatoms as O, S and/or N atoms. The effect of organic compounds containing polar groups and π-electrons on the corrosion behaviour of iron and steel has been well documented and showed to be quite efficient to prevent corrosion. The inhibiting action of those organic compounds is usually attributed to interactions with metallic surfaces by adsorption through lone pair of electrons of heteroatoms. The polar function is frequently regarded as the reaction centre for the adsorption process establishment. The adsorption bond strength depends on the electron density and polarizability of the functional group. The existing data show that most organic inhibitors are adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier film [(228)].

Chemisorbed organic molecules prevent steel corrosion by forming a chelate on the metal surfaces and the inhibition efficiency of an inhibitor are depended strongly on the chemical structure or the functional groups on the inhibitor molecule [(229)].

The aim of this work is to prepare and evaluate some thiol compounds as long-term organic corrosion inhibitors in such a manner that they are safe, cheap, efficient and compatible with water-borne coatings.

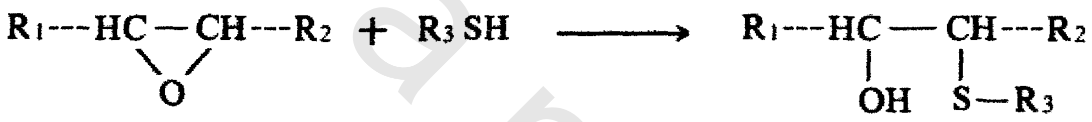
Part 1

Preparation and emulsification of some sulfur adducts

4.1.1. Preparation of inhibitors

4.1.1.1. Reaction of epoxidized soybean oil with thiol compounds

For the preparation of inhibitor adducts, the epoxidized soybean oil were subjected to react with 2-mercapto-Δ^2-thiazoline (2-MT), 2-mercapto-benzothiazole (2-MBT), 2-mercapto-5-methyl-1, 3, 4-thiadiazole (2-MMT), and 3-mercapto-4-methyl-4H-1,2,4-triazole (3-MMT) stoichiometrically. The reactions were pressured to proceed according to the following equation [230]:



The reactions between the epoxidized soybean oil and organic thiols were carried out in double wall sealed ampoules under inert atmosphere at 110-190 °C (according to melting point of each compound) for (4-6 hours).

The prepared adducts were mixed with different organic solvents; it was found that the sulfur adducts were freely soluble in benzene, toluene, xylene, acetone and ethyl acetate. This means that no cross-linking has been occurred during the reaction.

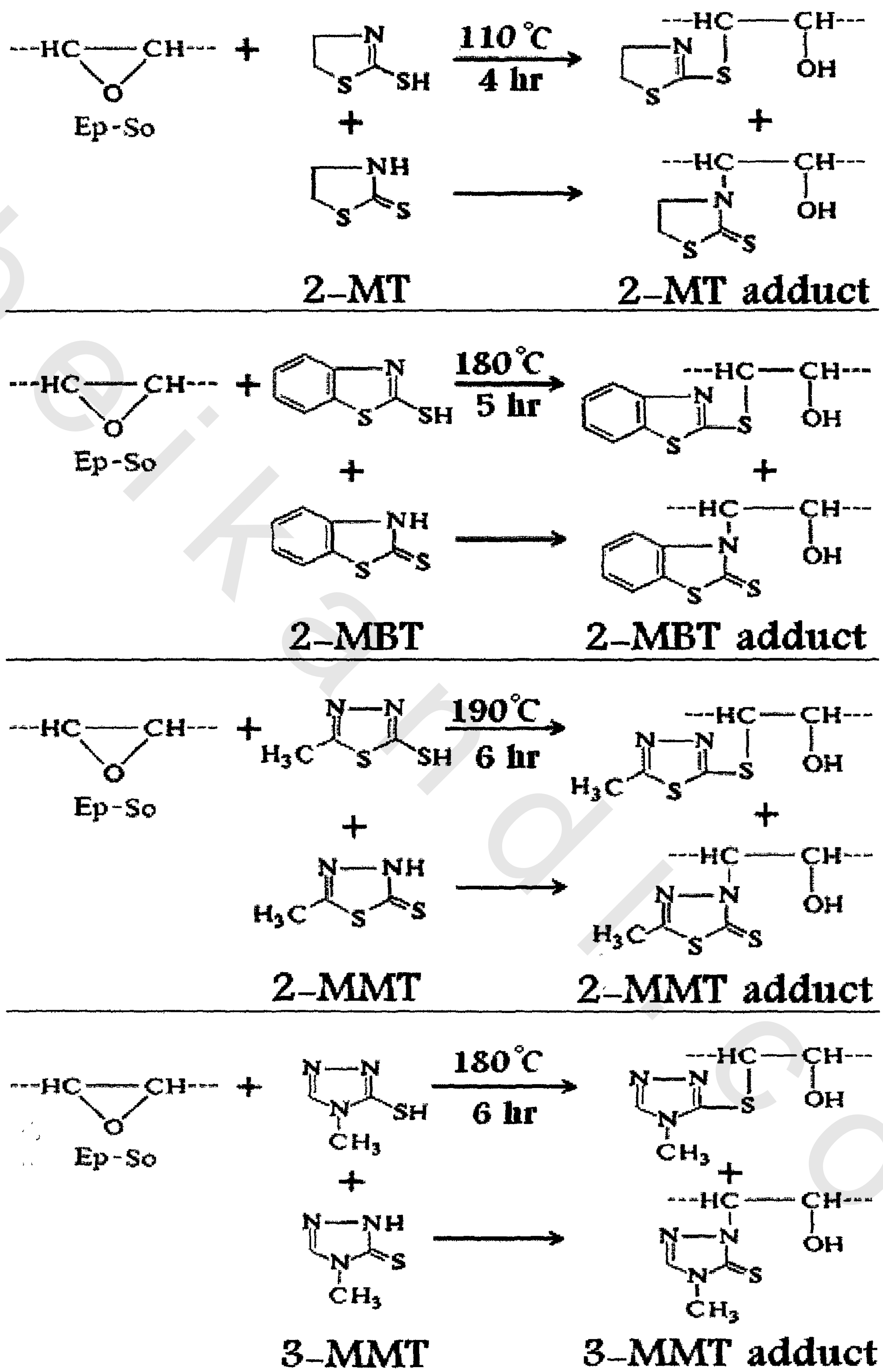


Fig. (4.1): Preparation of sulfur adducts

4.1.1.2. Characterization of the prepared adducts

4.1.1.2. a. Infra-red spectroscopy

Soybean oil, organic sulfur compounds, and their reaction products were characterized, physically, by using infra-red spectroscopy (IR) technique to confirm the formation of the desired adducts, as shown in Figure s (4.2 - 4.6).

Regarding to Figure (4.2), it had been turned out that a characteristic band of epoxy group appeared at 825 cm^{-1}. The ester group exhibited two bands, a strong band at 1743 cm^{-1} due to (C=O) group and a broad band at 1160 cm^{-1} due to (C-O) group. Also, there was a strong band at 2855 cm^{-1} due to (C-H) stretching attached to the ester group.

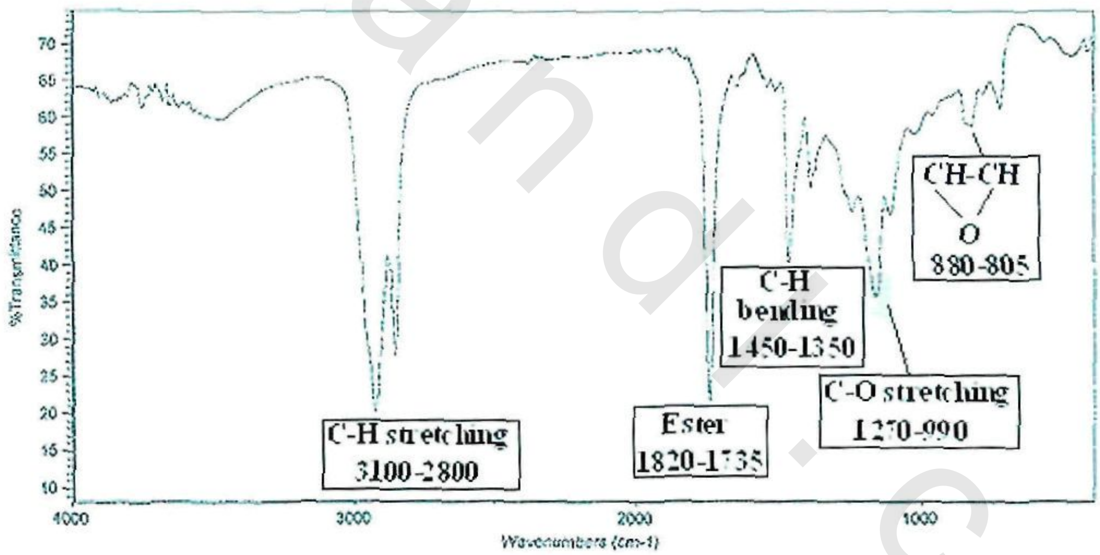


Fig. (4.2): (IR) Chart of epoxidized soybean oil

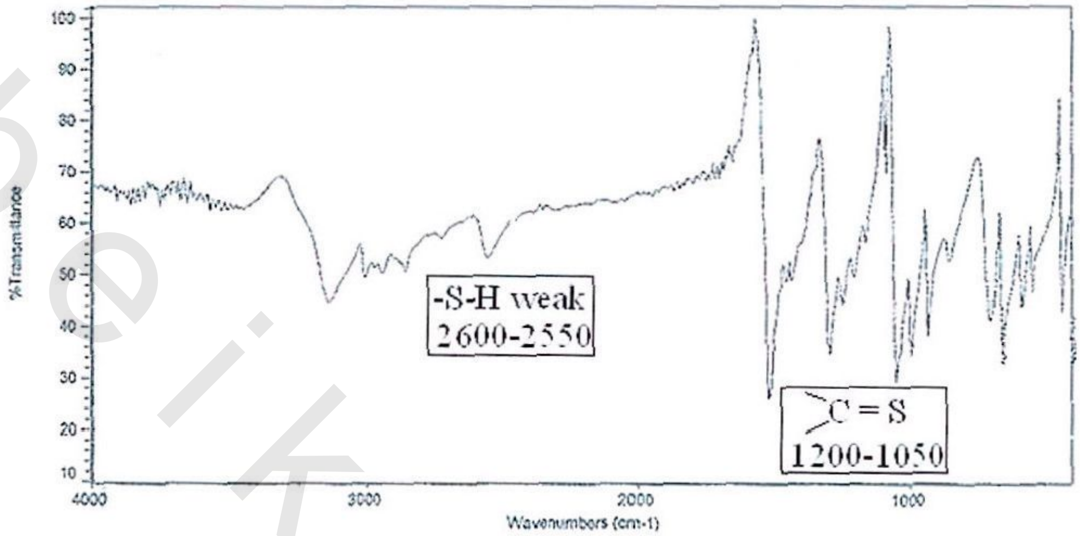


Fig. (4.3a): (IR) Chart of 2-mercapto-Δ^2-thiazoline

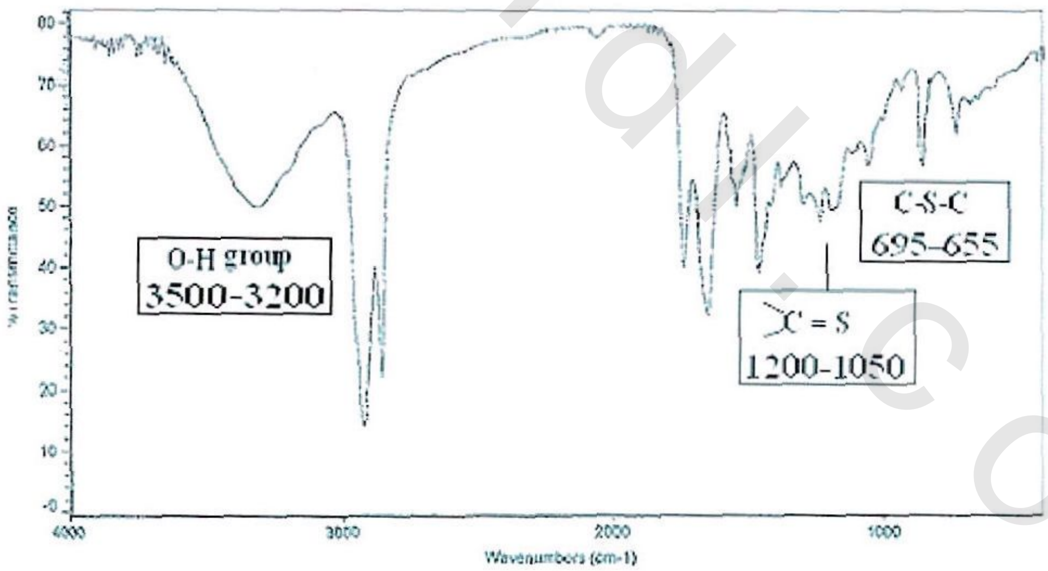


Fig. (4.3b): (IR) Chart of 2-mercapto-Δ^2-thiazoline adduct

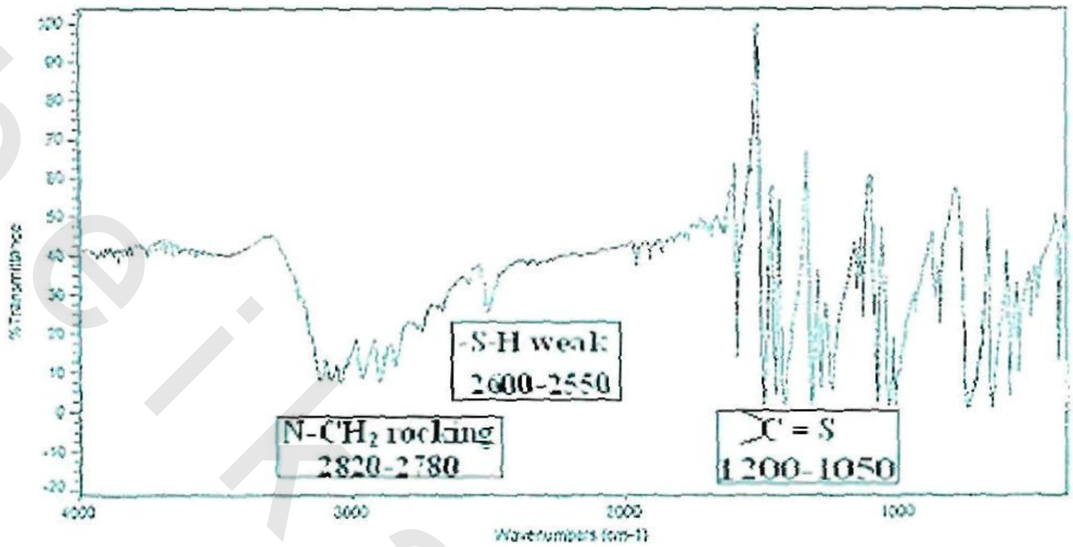


Fig. (4.4a): (IR) Chart of 2-mercaptobenzothiazole

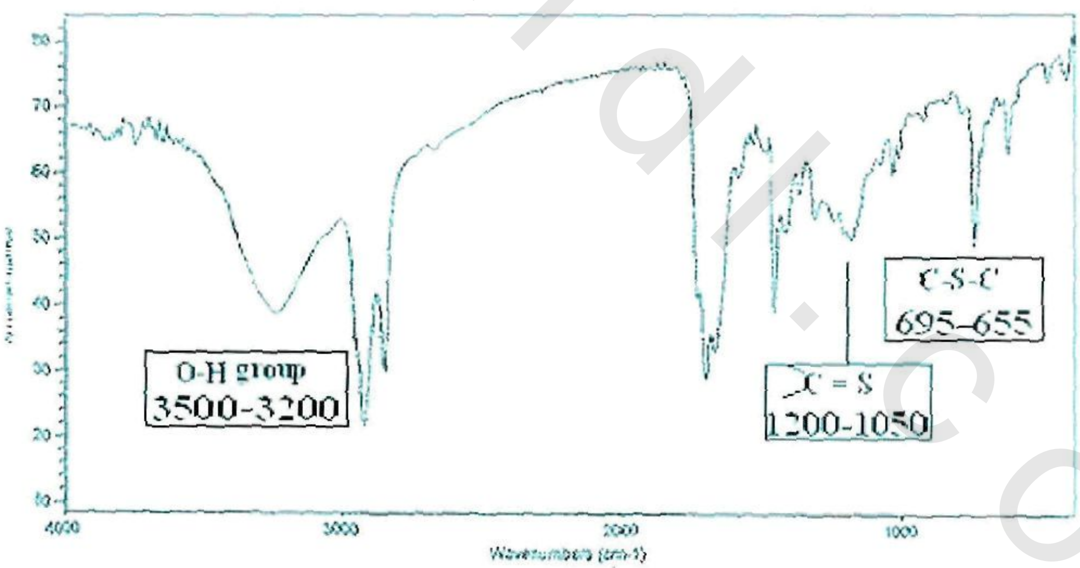


Fig. (4.4b): (IR) Chart of 2-mercaptobenzothiazole adduct

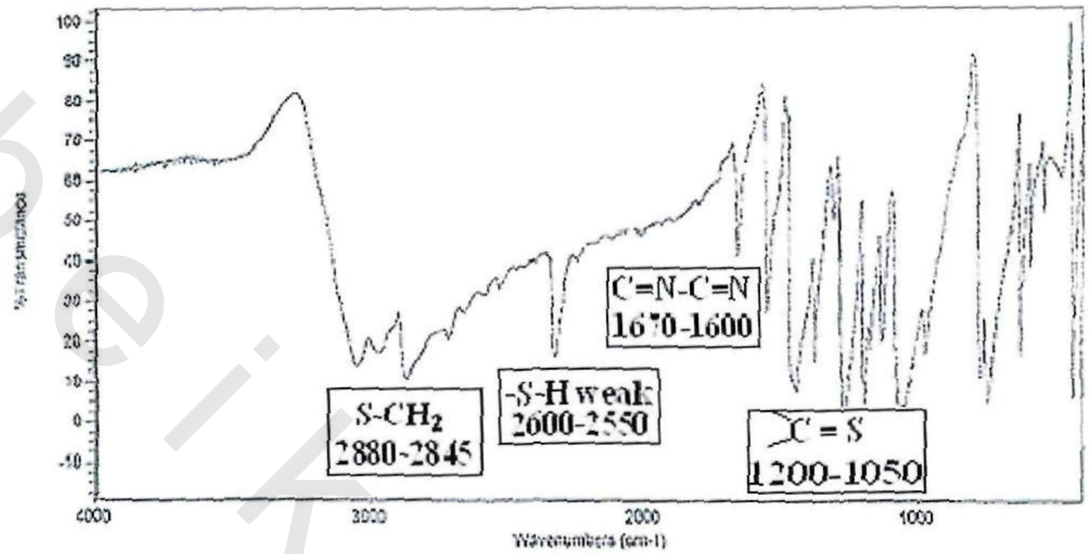


Fig. (4.5a): (IR) Chart of 2-mercapto-5-methyl-1, 3, 4-thiadiazole

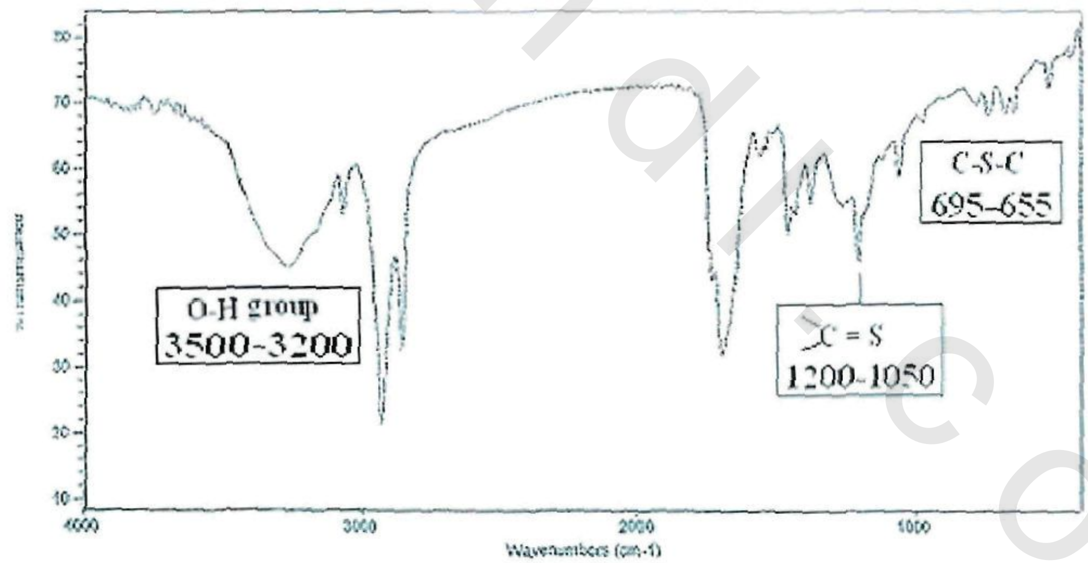


Fig. (4.5b): (IR) Chart of 2-mercapto-5-methyl-1, 3, 4-thiadiazole adduct

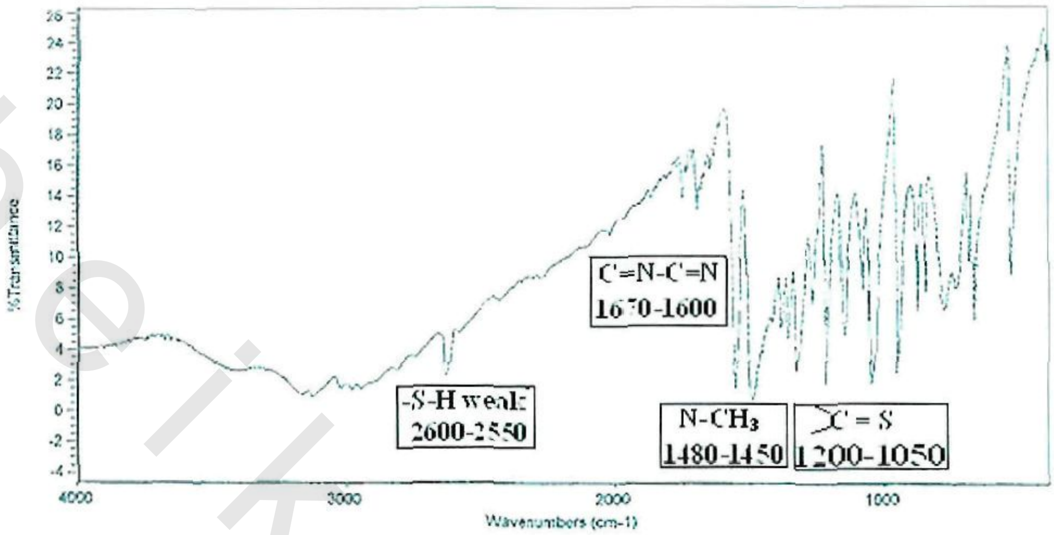


Fig. (4.6a): (IR) Chart of 3-mercapto-4-methyl-4H-1, 2, 4-triazole

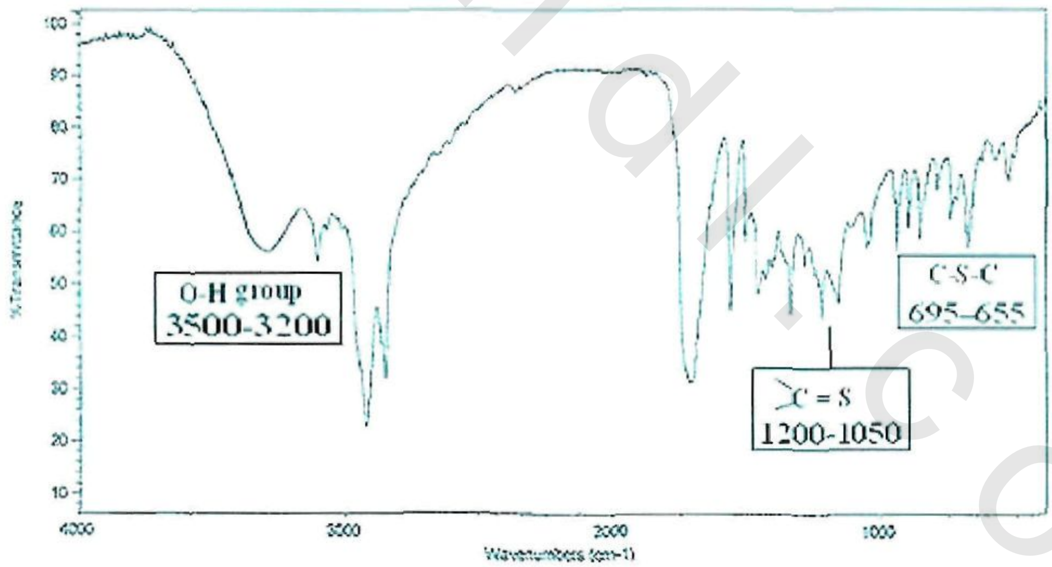


Fig. (4.6b): (IR) Chart of 3-mercapto-4-methyl-4H-1, 2, 4-triazole adduct

Figures (4.3a), (4.4a), (4.5a) and (4.6a) show the IR spectra of thiols. It was noticed that all compounds revealed a weak peak at 2600-2550 cm^{-1}, due to (-SH) group, and band at 1200-1050 cm^{-1} due to (C=S) thione group. Table (4.1) shows the characteristic spectral data analysis of the reacting thiols.

Figures (4.3b), (4.4b), (4.5b) and (4.6b) show the IR spectra of the soybean oil/thiol adducts. Generally, all products revealed that the disappearance of the characteristic bands of starting materials (i.e. the epoxy band at 880-805 cm^{-1}, and thiol group band at 2600-2550 cm^{-1}), and appearance new band at 3500-3200 cm^{-1} due to (O-H) group, and band at 695-655 cm^{-1} stretching due to (C-S-C) group . Table (4.2) shows the characteristic IR spectral bands of thiol adducts.

Table (4.1): IR Characteristic peaks for starting materials

Compounds	Characteristic peaks
Epoxidized soybean oil	Epoxy group at 825.83 cm^{-1}, C-O at 1160.86 cm^{-1}, ester group at 1743.39 cm^{-1}.
2-mercapto-Δ^2-thiazoline	Thione band at, 1200-1050 cm^{-1}, -SH group at 2600-2550 cm^{-1}, $N-CH_2$ at 2820-2700 cm^{-1}.
2-mercaptobenzothiazole	Thione band at, 1200-1050 cm^{-1}, -SH group at 2600-2550 cm^{-1}, $N-CH_2$ at 2820-2700 cm^{-1}.
2-mercapto-5-methyl-1, 3, 4-thiadiazole	Thione band at, 1200-1050 cm^{-1}, -SH group at 2600-2550 cm^{-1}, $S-CH_2$ at 2880-2845 cm^{-1}, C=N-N=C at 1670-1600 cm^{-1}.
3-mercapto-4-methyl-4H-1, 2, 4-triazole	Thione band at, 1200-1050 cm^{-1}, -SH group at 2600-2550 cm^{-1}, C=N-N=C at 1670-1600 cm^{-1}, $N-CH_3$ at 1480-1450 cm^{-1}.

Table (4.2): IR Characteristic peaks for thiol adducts

Compounds	Characteristic peaks
2-mercapto-Δ^2-thiazoline adduct	C-S-C band, at 758.32 cm^{-1}, thione band at, 1200-1050 cm^{-1}, O-H broad band at, 3311.65 cm^{-1}.
2-mercaptobenzothiazole adduct	C-S-C band, at 747.18 cm^{-1}, thione band at, 1200-1050 cm^{-1}, O-H broad band at, 3351.28 cm^{-1}.
2-mercapto-5-methyl-1, 3, 4-thiadiazole adduct	C-S-C band, at 732.82 cm^{-1}, thione band at, 1200-1050 cm^{-1}, O-H broad band at, 3362.38 cm^{-1}.
3-mercapto-4-methyl-4H-1, 2, 4-triazole adduct	C-S-C band, at 746.24 cm^{-1}, thione band at, 1200-1050 cm^{-1}, O-H broad band at, 3392.84 cm^{-1}.

4.1.1.2. b. Gel permeation chromatography (GPC)

The theoretical molecular weight (M.wt), weight-average molecular weight ($\overline{M}_w$), number average molecular weight ($\overline{M}_n$) and polydispersity (PDI = $\overline{M}_w/\overline{M}_n$) of (Ep-So, 2-MT, 2-MBT, 2-MMT and 3-MMT adducts) are summarized in Table (4.3).

Table (4.3): Molecular weight measurements

Sample	Theoretical M.wt, g/mol	$\overline{M}_w$, g/mol	$\overline{M}_n$, g/mol	PDI
Ep-So	1000	1226.3	845.35	1.451
2-MT adduct	1476	1572.3	229.65	6.8465
2-MBT adduct	1668	1781.3	1563.4	1.1393
2-MMT adduct	1528	1740.2	446.52	3.8972
3-MMT adduct	1460	1493.5	1140.0	1.3100

It can be seen from Table (4.3), that the GPC M.wt of (Ep-So, 2-MT, 2-MBT, 2-MMT and 3-MMT adducts) approximately equivalent to theoretical M.wt. This means that the reaction between epoxidized soybean oil and organic thiols proceeded successfully without by-products.

4.1.2. Emulsification of the prepared adducts

An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases, one of which is dispersed as droplets in the other. The thermodynamic instability of emulsion systems is a consequence of the high interfacial free energy that exists between the two phases. This free energy is the driving force for droplet coalescence and eventual phase separation. Surfactants are added to improve emulsion stability by decreasing interfacial free energy and providing a mechanical barrier to droplet coalescence. Generally, the most stable emulsion systems consist of blends of two or more emulsifiers with different ratios to achieve the exact hydrophilic-lipophilic balance (HLB) value required for emulsification. Only in relatively rare cases, a single emulsifier may be used, even though it might have the exact HLB value for emulsification [106].

The aim of this part is to obtain stable emulsified adducts in order to be suitable to water-borne paint. The continuous phase is distilled water/Tween 20 and the dispersed phase is the prepared adduct (oil)/xylene/Span 20/Span 80.

4.1.2.1. Critical micelle concentrations of Tween 20

It is interesting to study the critical micelle concentration (C.M.C) of Tween 20 in distilled water, which gives minimum surface tension. Thus, a series of different concentrations from 0.0 to 1.0 gm Tween 20 per 100 ml distilled water were prepared. Surface tension of each concentration was measured at 20 °C using Krüss tensiometer. The obtained results are given in Table (4.4) and represented graphically in Figure (4.7).

Table (4.4): Critical micelle concentrations of Tween 20

Conc. Of T20, %	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\sigma^{(1)}$, mN/m	72.3	42.1	40.6	40.1	39.2	38.9	39.1	39.75	40.1	40.3	40.6

1. *$\sigma = \sigma^* \times F$, where σ is the actual value of interfacial tension; σ^* is the measured value of interfacial tension; F is the correction factor, which equal to the quotient of the theoretical and indicated value of distilled water.*

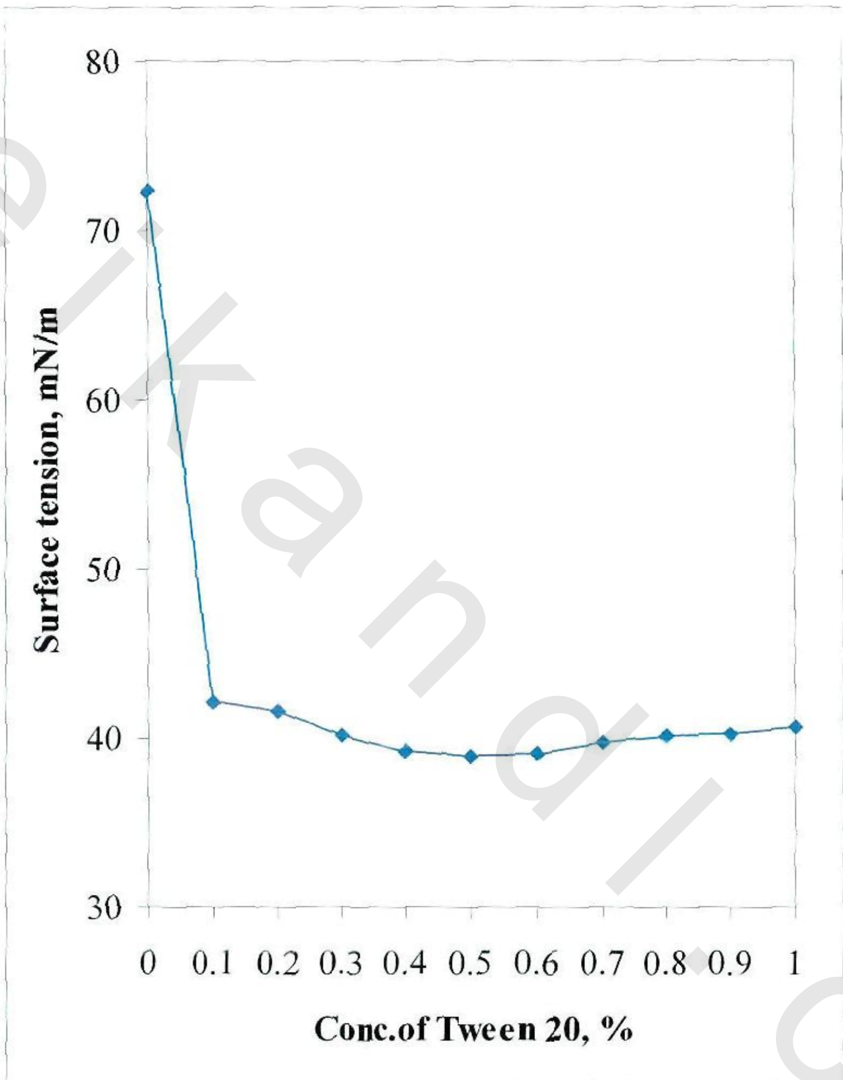


Figure (4.7): Effect of Tween 20 concentrations on the surface tension of distilled water

Both Table (4.4) and Figure (4.7) show that the surface tension of Tween 20 in 100 ml of distilled water decreased sharply by addition 0.1% Tween 20, then decreases gradually by addition of Tween 20 to 0.5%, after this concentration the change in surface tension was very limited.

From these results, the concentration of 0.5 gm of Tween 20 in 100 ml distilled water is the most efficient concentration at which the lowest surface tension has been obtained. Consequently, 0.5% is the most suitable concentration to emulsify adducts in water.

4.1.2.2. Influence of the use of multiple surfactants on emulsion stability

Porras et al [(200)] proved that mixture of surfactants as Span 20, Span 80, Tween 20 and Tween 80 can provide better performance than pure surfactant, for water-in-oil emulsions.

The nonionic surfactant, polyoxyethylene (20) sorbitan monolaurate (T20), sorbitan monolaurate (S20) and sorbitan monooleate (S80) were selected because they form relatively stable emulsions of oil in water [(231)].

The HLB value of a combination of emulsifiers can be calculated as follows [(232 - 234)]:

$$\text{HLB} = \frac{\text{Quantity of surfactant 1)(HLB surfactant 1)} + \text{(Quantity of surfactant 2) (HLB surfactant 2)}}{\text{Quantity of surfactant 1} + \text{Quantity of surfactant 2}}$$

In the present work, 2 gm of 2-MT adduct was added drop by drop to 98 gm of 0.5% Tween 20/ distilled water during stirring using homogenizer with agitation rate 4000 r.p.m, and for 20 minutes at room temperature. In a second step 0.5 gm Span 20 and /or 0.5 g Span 80 was used. Surface tension and stability of each prepared emulsion were determined. Table (4.5) summarizes the obtained results.

Table (4.5): Effect of emulsifier type on emulsion stability

Emulsion No.	Emulsifier composition T20: (S20: S80)	HLB	σ, mN/m	Emulsion stability
1	0.5: (0.0: 0.0)	16.7	58.82	1 month
2	0.0 :(0.5: 0.0)	8.6	64.94	Unstable
3	0.0 :(0.0: 0.5)	4.3	68	Unstable
4	0.0 :(0.5: 0.5)	6.45	58.65	1 month
5	0.5 :(0.5: 0.0)	12.65	59.5	1 month
6	0.5 :(0.0: 0.5)	10.5	57.8	2 months
7	0.5: 0.5: 0.5	9.9	57.3	3 months

It is clear from the above results that the addition of Span 20 (HLB = 8.6) and Span 80 (HLB = 4.3) to Tween 20 (HLB = 16.7) improved the emulsion stability. The emulsion, which obtained by using a 0.5% of Tween 20 and blend of Span 20: Span 80 by ratio 1:1(calculated HLB = 9.9), gave minimum surface tension (57.3 mN/m) and stable for 3 months.

This result goes hand in hand with the fact that the use of mixture of emulsifiers would result in emulsions of varying degrees of stability. This can be attributed to the degree of structure similarity between the hydrocarbon moieties of adduct and emulsifiers. Also combination of emulsifiers can produce more stable emulsions than using a single emulsifier with the same HLB number.

4.1.2.3. Effect of solvent and pH on surface tension and emulsion stability

In this study 2-MT adduct has been emulsified in absence and presence of xylene and/ or ammonium hydroxide. The continuous phase is 0.5% Tween 20/ distilled water/ ammonium hydroxide. The dispersed phase is adduct/xylene/span blend. Emulsion stability and surface tension of emulsion formulations have been studied and summarized in the following Table (4.6)

Table (4.6): Effect of solvent and pH

Emulsion No.	Solvent	pH	σ, mN/m	Emulsion stability
7	---	---	57.3	3 months
8	Xylene	---	55.9	4 months
9	---	≥8	56.2	4 months
10	Xylene	≥8	54.9	6 months

From the above Table, it is clear that the emulsion No. 10 is stable for 6 months and have less surface tension value than emulsions No. 7, 8, and 9, this due to alkaline pH, which reduces surface tension value. This result goes hand in hand with the fact that the alkaline pH reduces the tensile strength of particle size of emulsion, and hence reduces the surface tension value.

Also at alkaline pH the electrostatic repulsion between the droplets was sufficiently strong to prevent droplet coalescence and consequently increase emulsion stability. The improvement of emulsion stability in case of solvent addition may be related to its effect on reducing interfacial tension between the dispersed phase and continuous phase, so that the increase in interfacial area is reduced.

4.1.2.4. Effect of adduct concentration and emulsifier concentration on surface tension and emulsion stability

To prepare stable emulsion with high concentration of the prepared 2-MT adduct, many trials have been done using the same previous technique of emulsification. The continuous phase 0.5% Tween 20/ distilled water/ ammonium hydroxide, and the dispersed phase adduct/xylene/span blend by ratio 1:1 were used. The emulsification of 2, 5, 10, 15, and 20% wt/wt of 2-MT adduct was carried out by different concentrations of span blend, taking into consideration constant 1:1 ratio to obtain emulsion with high stability. The obtained results are summarized in Table (4.7).

Table (4.7): Effect of adduct concentration and emulsifier concentration on the prepared emulsions

Emulsion No.	Oil content	Total conc. of span in blend ,g	σ, mN/m	Emulsion stability
10	2%	1	54.9	6 months
11	5%	1	55.1	4 months
12	5%	2	54.6	6 months
13	10%	2	56	4 months
14	10%	4	54.5	6 months
15	15%	4	55.3	4 months
16	15%	6	54.4	6 months
17	20%	6	55.3	4 months
18	20%	8	54.5	6 months

Table (4.7) showed that the preparation of high concentration emulsion adduct up to 20% , requires higher concentration (8 gm) of span blend which represents 40% of the total adduct content.

These results go parallel to those obtained by *Dimitrov* and *Ivanov* [235, 236]; where they suggested that, higher concentrations of surface active agents (emulsifier) should increase emulsion stability through a number of complementary factors.

4.1.2.5. Emulsification of different sulfur adducts

To prepare stable emulsion with 20% (wt/wt) of the prepared adducts [2-mercapto-Δ^2-thiazoline (2-MT), 2-mercaptobenzothiazole (2-MBT), 2-mercapto-5-methyl-1, 3, 4- thiadiazole (2-MMT), and 3-mercapto-4-methyl- 4H-1, 2, 4- triazole (3-MMT)], many trials have been done using different concentrations of span blend, keeping constant ratio (1:1). The continuous phase is 0.5% Tween 20/ distilled water/ ammonium hydroxide, and the dispersed phase is adduct/xylene/span blend with different concentrations and ratio 1:1.The obtained results are summarized in Table (4.8)

Table (4.8): Emulsification of different adduct types

Emulsion No.	Adduct type (20%)	Total span conc.	Conc. of span blend with respect to adduct, %	σ, mN/m	Emulsion stability
18	2-MT	8	40	54.5	6 months
19	2-MT	9	45	54.3	6 months
20	2-MT	10	50	54.0	6 months
21	2-MBT	8	40	55.2	5 months
22	2-MBT	9	45	54.6	6 months
23	2-MBT	10	50	54.2	6 months
24	2-MMT	8	40	57.4	3 months
25	2-MMT	9	45	55.8	4 months
26	2-MMT	10	50	54.5	6 months
27	3-MMT	8	40	57.5	3 months
28	3-MMT	9	45	56	4 months
29	3-MMT	10	50	54.5	6 months

The above results show that, to achieve 6 months stability for 2-MT adduct, an amount of 40% (wt/wt) of span blend is required; while this amount jumped to 45 % for 2-MBT and 50% for 2-MMT and 3-MMT adducts.

Conclusions

- The reaction between epoxidized soybean oil and thiol compounds had taken place successfully, and neither cross-linking nor formation of by-products during the reaction has been occurred.
- The reaction products were relatively high molecular weight adducts and they have suitable characteristics which may inhibit corrosion of mild steel.
- Critical micelle concentration (C.M.C.) of Tween 20 in pure distilled water was 0.5% (wt /wt).
- Combination of emulsifiers can produce more stable emulsion than using a single emulsifier with the same HLB value.
- Alkaline pH reduced surface tension values and increases the emulsion stability.
- The best emulsion stability of 20% oil in water (O/W) was obtained by using C.M.C. of Tween 20 and 8-10g blend of Span 20 and Span 80 emulsifiers by ratio 1:1 at pH $\geq$8.

Part 2

The emulsified adducts as corrosion inhibitors

As discussed in part (1), the reaction products of epoxidized soybean oil with thiol compounds have been emulsified in water in order to be compatible with water-borne paint formulations.

In this part, the prepared adducts are evaluated as corrosion inhibitors for mild steel. This part comprises five groups:

Group I

The aim of this group is to optimize different blank formulations and maximize the barrier function of the prepared paint, which contain no corrosion inhibitors.

Group II

Group II aims to optimization of different concentrations of the prepared 2-mercapto-Δ^2-thiazoline adduct as a model of the prepared corrosion inhibitors in water-borne paint formulations based on urabrid AC100 emulsion free of anti-corrosive pigments.

Group III

This group aims to arrange the prepared emulsified adducts 2-mercapto-Δ^2-thiazoline (2-MT), 2-mercaptobenzothiazole (2-MBT), 2-mercapto-5-methyl-1, 3, 4-thiadiazole (2-MMT), and 3-mercapto-4-methyl-4H-1, 2, 4- triazole (3-MMT) according to their efficiencies as corrosion inhibitor for mild steel using the optimum concentration of 2-MT adduct.

Group IV

In this group, three types of emulsion binders were used, (acrylic, short oil alkyd and urabrid AC100 emulsion resins) in order to study the effect of resin type on long-term corrosion resistance of anti-corrosive coatings using 3-MMT adduct as a sole corrosion inhibitor.

Group V

Finally group aims to compare the corrosion inhibition performance of urabrid AC100 coatings formulated with 3-MMT organic inhibitor, with the most commonly used anti-corrosive pigment zinc phosphate as barrier/ inhibitive pigment and zinc chromate as an inhibitive pigment.

4.2.1. Group I: Paint formulations free of the prepared adducts

The aim of this group is to optimize the different blank formulations and maximize the barrier function of the prepared paint, which contain no corrosion inhibitors. The influence of pigment binder ratio on some coating properties such as water uptake, blistering resistance and rusting of metal surface under paint film was the main approach.

Group I consists of three series of different paint formulations (A, B and C). Each series includes six paint formulations for each binder type. The binder in series A is acrylic emulsion resin, and urabrid AC100 emulsion resin in series B, while short oil alkyd emulsion resin was used in series C. The mill base composition is the same in all above mentioned series, where titanium dioxide was used as a neutral pigment and talc as an extender. The composition of the white mill base is shown in Table (4.9).

Emulsion paint formulations for this group of series A, B and C were represented in Tables (4.10, 4.11 and 4.12), respectively.

Table (4.9): Composition of mill base I

Component	Weight, %
Titanium dioxide (Rutile)	38.60
Talc	26.40
Dispersing /wetting agent	1.53
Anti-foaming agent	0.40
Ethanol amine	1.0
Water	32.07
Total weight	100

Formulation constants:

Solid content by weight	65%
pH	≥8
Fineness of mill base	< 10 μm

Table (4.10): Emulsion paint formulation of series A

Composition \ Formula No.	A1	A2	A3	A4	A5	A6
Mill base (I)	26.2	31.4	36.62	41.9	47.1	52.31
Acrylic emulsion	30.91	30.91	30.91	30.91	30.91	30.91
Additives (*)	9.0	8.8	8.6	8.4	8.2	8.0
Water	33.89	28.89	23.87	18.79	13.79	8.78
Total weight	100	100	100	100	100	100
Pigment binder ratio	1.0	1.2	1.4	1.6	1.8	2.0

(*) The additives involve: butyl glycol, texanol, iso-propanol, ethanol amine, flash rust inhibitor, biocide, anti-foaming agent and thickener.

Table (4.11): Emulsion paint formulation of series B

Composition \ Formula No.	B1	B2	B3	B4	B5	B6
Mill base (I)	26.2	31.4	36.62	41.9	47.1	52.31
Urabrid AC100	39.54	39.54	39.54	39.54	39.54	39.54
Additives (*)	8.6	8.6	7.5	6.5	5.2	4.5
Water	25.66	20.46	16.34	12.06	8.16	3.65
Total weight	100	100	100	100	100	100
Pigment binder ratio	1.0	1.2	1.4	1.6	1.8	2.0

(*) The additives involve: butyl glycol, texanol, iso-propanol, ethanol amine, flash rust inhibitor, drier, biocide, anti-foaming agent and thickener.

Table (4.12): Emulsion paint formulation of series C

Composition \ Formula No.	C1	C2	C3	C4	C5	C6
Mill base (I)	26.2	31.4	36.62	41.9	47.1	52.31
Alkyd emulsion	37.8	37.8	37.8	37.8	37.8	37.8
Additives (*)	8.5	8.0	7.5	6.5	5.5	4.5
Water	27.5	22.8	18.08	13.8	9.6	5.39
Total weight	100	100	100	100	100	100
Pigment binder ratio	1.0	1.2	1.4	1.6	1.8	2.0

(*) The additives involve: butyl glycol, texanol, iso-propanol, ethanol amine, flash rust inhibitor, drier, biocide, anti-foaming agent and thickener.

The physical, chemical and mechanical tests are shown in Tables (4.13, 4.14 and 4.15), for all paint formulations of group I.

Table (4.13): Physical, chemical and mechanical properties of paint films of series A

Test \ Formula No.	A1	A2	A3	A4	A5	A6
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	F	H	2H	3H	3H	4H
Ductility	7.3	7.1	6.9	6.9	6.8	6.6
Bending	Pass	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

Table (4.14): Physical, chemical and mechanical properties of paint films of series B

Test \ Formula No.	B1	B2	B3	B4	B5	B6
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	H	2H	2H	4H	5H	6H
Ductility	6.2	6.2	6.3	6.2	6.1	6.1
Bending	Pass	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

Table (4.15): Physical, chemical and mechanical properties of paint films of series C

Test \ Formula No.	C1	C2	C3	C4	C5	C6
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	2H	2H	3H	4H	5H	6H
Ductility	6.5	6.3	6.2	6.2	6.1	6.1
Bending	Pass	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

It is clear from the above Tables, that the hardness of the paint films of group (I) slightly increases by increasing pigment binder ratio as predicted. All films of the investigated formulations showed high adhesion to steel panels and excellent flexibility (bending and ductility). Also, the prepared paint films succeeded to pass acid, alkali and water resistance tests.

Water up-take measurements are given in Tables (4.16, 4.17 and 4.18), and plotted in Fig. (4.8).

Table (4.16): Water up-take (%) for paint films of series A

Time (days) / Formula No.	5	10	15	20	25	30
A1	7.78	10.42	14.61	16.31	18.10	18.63
A2	9.28	11.18	15.16	17.62	19.23	20.11
A3	6.39	10.50	13.36	15.70	16.05	17.52
A4	5.84	8.82	11.06	13.21	15.53	16.23
A5	9.30	10.55	12.61	15.80	18.04	19.47
A6	15.29	17.66	19.18	20.04	21.16	22.51

Table (4.17): Water up-take (%) for paint films of series B

Time (days) / Formula No.	5	10	15	20	25	30
B1	15.21	17.40	20.36	21.17	23.51	24.37
B2	14.11	16.60	18.23	19.51	21.25	23.16
B3	15.34	17.81	20.71	22.43	24.18	25.56
B4	12.27	14.46	16.36	18.95	21.50	23.12
B5	11.23	13.35	15.65	18.16	19.94	21.11
B6	13.52	15.06	18.77	20.18	22.82	24.18

Table (4.18): Water up-take (%) for paint films of series C

Time (days) / Formula No.	5	10	15	20	25	30
C1	7.72	10.86	12.65	13.71	15.44	16.55
C2	8.15	10.54	11.87	12.14	13.31	14.95
C3	7.00	10.82	12.43	13.65	14.56	15.42
C4	5.53	8.41	10.13	11.52	13.47	14.64
C5	3.87	5.33	8.60	10.73	12.62	13.41
C6	3.11	5.61	8.26	10.45	12.95	14.77

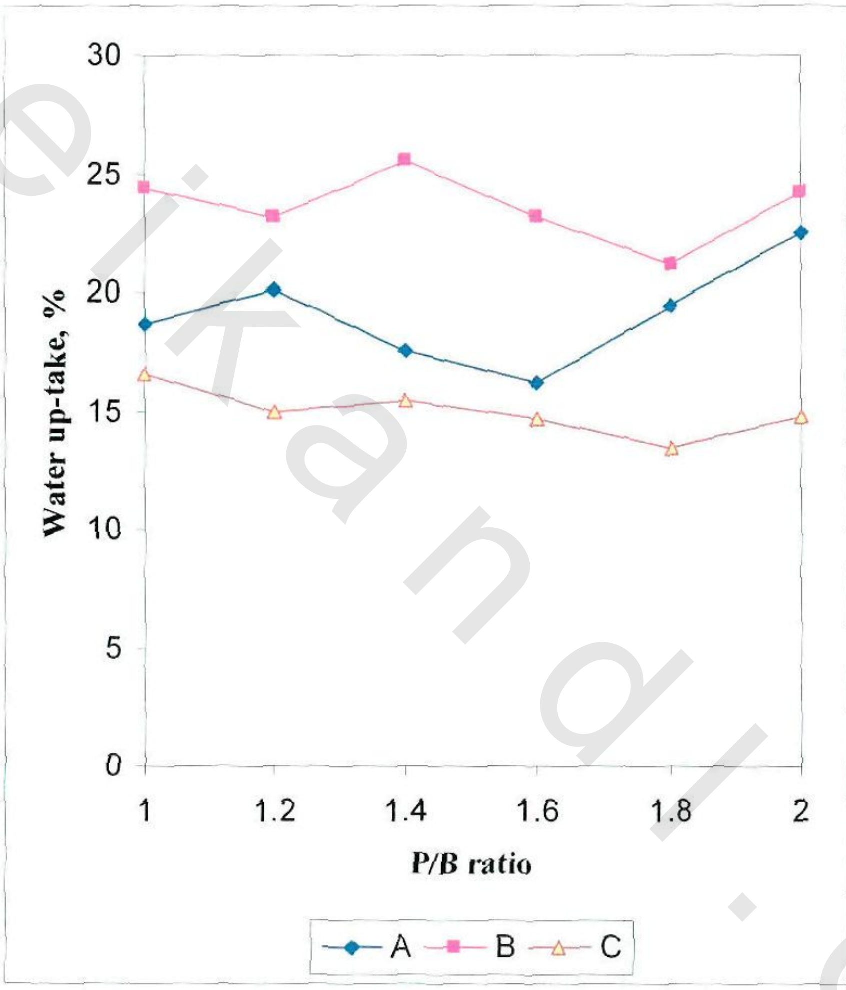


Figure (4.8): The variation in water up-take (%) with different P/B ratios

The data obtained in Tables (4.16, 4.17 and 4.18) and Fig. (4.8) show that the formula A4 have minimum water up-take, after 30 days immersion in distilled water, while maximum water up-take in series A was observed at formula A6. In series B, the minimum water up-take was observed with formula B5, also in series C, it was found formula C5 have minimum water up-take. From these results, it can be concluded that there is a strong dependence of water up-take of a coating on pigment binder ratio and on the type of used binder.

The results of corrosion resistance tests of series A, B and C are given in Tables (4.19, 4.20 and 4.21). The painted metal plates were detected for blistering resistance of coating films, failure around the scribe and the degree of rusting of metal surface under paint films, after immersion of the painted metal plates of these series in artificial sea water for 28 days. Figures (4.9, 4.10, and 4.11) represent photos of metal plates failure around the scribe and degree of rusting of metal surface, after 28 days immersion in sea water.

Table (4.19): Corrosion resistance tests for paint films of series A

Test \ Formula No.	A1	A2	A3	A4	A5	A6
Corrosion resistance (1)	s.t.	m.t.	m.t.	c	h.t.	m.t.
Degree of blistering (2)	10	8M	8M	10	6MD	9F
Corrosion scratch test (3)	D	E	D	A	E	C

Table (4.20): Corrosion resistance tests for paint films of series B

Test \ Formula No.	B1	B2	B3	B4	B5	B6
Corrosion resistance (1)	h.t.	s.t.	m.t.	s.t.	s.t.	s.t.
Degree of blistering (2)	9F	10	9F	8F	8F	8F
Corrosion scratch test (3)	F	F	E	B	B	B

Table (4.21): Corrosion resistance tests for paint films of series C

Test \ Formula No.	C1	C2	C3	C4	C5	C6
Corrosion resistance (1)	h.t.	s.t.	c	c	b	c
Degree of blistering (2)	5MD	8F	9F	6M	10	10
Corrosion scratch test (3)	C	D	D	A	A	A

1. ***b:*** Bright surface; ***c:*** clean; ***v.s.t***: very slight tarnishing; ***s.t.:*** slight tarnishing; ***m.t.:*** medium tarnishing; ***h.t.***: high tarnishing and ***h.t.p.:*** high tarnishing and pitting.
2. It is graded on a scale from ***10*** to ***0***, where ***10*** no blistering and ***0*** for largest blisters and frequency denoted by ***F, M, MD*** and ***D*** (few, medium, medium dense and dense) respectively.
3. ***A-E***: Corrosion just in the scratch but differs in the adhesion of the film around the scratch; ***A = Gt0, B = Gt1, C = Gt2, D = Gt3, E = Gt4.***

With respect to series A formulations which contain acrylic resin, the obtained results show that the best corrosion resistance was obtained using pigment binder ratio 1.6 (Formula A4), while the other formulations showed severe corrosion, failure of adhesion around the scribe and higher degree of blistering. Series B formulations, which contain urabrid AC100 resin, show maximum corrosion resistance at pigment binder ratio 1.8 (Formula B5). Also, in series C formulations, which contain short oil alkyd resin, the maximum corrosion resistance was happen at pigment binder ratio 1.8 (Formula C5).

The weight loss variation of paint films of this group are given in Tables (4.22, 4.23 and 4.24) and plotted in Fig. (4.12).

Fig. (4.9): Corrosion progress under paint films of series A after 28 days immersion in artificial sea water

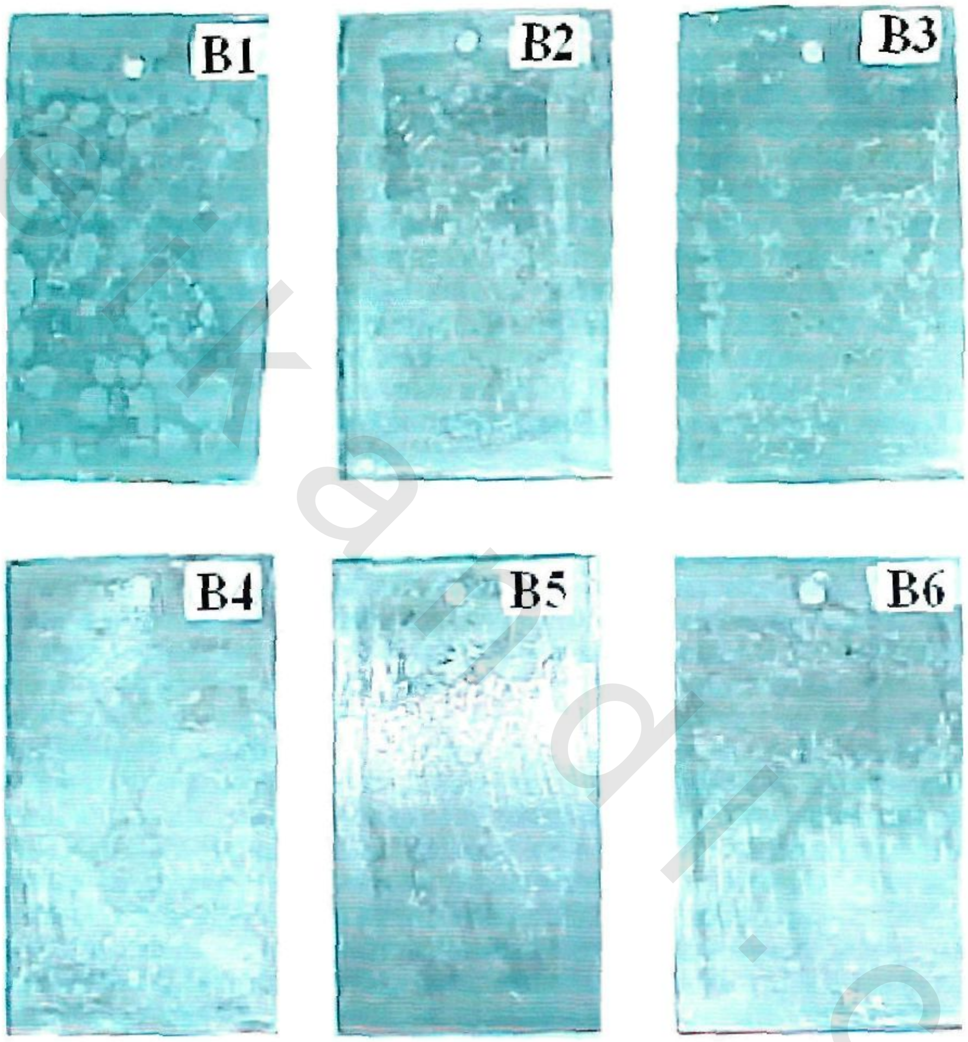


Fig. (4.10): Corrosion progress under paint films of series B after 28 days immersion in artificial sea water

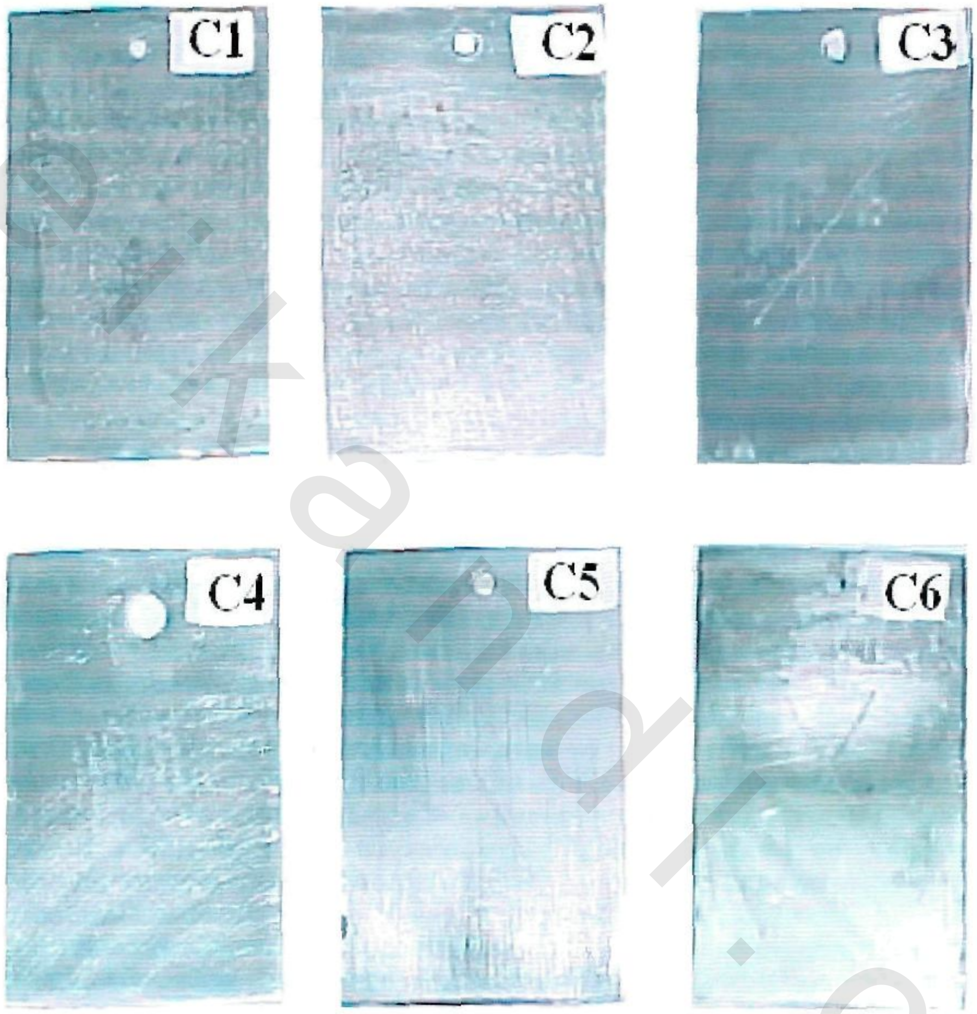


Fig. (4.11): Corrosion progress under paint films of series C after 28 days immersion in artificial sea water

Table (4.22): Weight loss measurements (mg/cm^2), for steel panels under paint films of series A

Formula No. \ Time (days)	10	20	30	40	50	60
A1	0.385	0.504	0.710	0.966	1.136	1.597
A2	0.522	0.771	0.906	1.276	1.515	1.664
A3	0.301	0.491	0.683	0.970	1.104	1.416
A4	0.349	0.516	0.702	0.911	1.122	1.367
A5	0.383	0.528	0.717	1.074	1.268	1.633
A6	0.512	0.780	0.963	1.254	1.503	1.784

Table (4.23): Weight loss measurements (mg/cm^2), for steel panels under paint films of series B

Formula No. \ Time (days)	10	20	30	40	50	60
B1	0.221	0.411	0.633	0.851	1.113	1.441
B2	0.116	0.296	0.436	0.665	0.974	1.213
B3	0.156	0.361	0.592	0.838	1.034	1.342
B4	0.214	0.448	0.678	0.891	1.169	1.203
B5	0.115	0.210	0.396	0.568	0.790	0.971
B6	0.203	0.361	0.556	0.703	0.991	1.264

Table (4.24): Weight loss measurements (mg/cm^2), for steel panels under paint films of series C

Formula No. \ Time (days)	10	20	30	40	50	60
C1	0.366	0.481	0.615	0.724	0.860	0.991
C2	0.138	0.261	0.403	0.516	0.642	0.782
C3	0.341	0.416	0.546	0.664	0.723	0.876
C4	0.130	0.192	0.253	0.416	0.528	0.760
C5	0.105	0.162	0.301	0.466	0.584	0.688
C6	0.216	0.316	0.451	0.515	0.604	0.701

From the above results, it is clear that, the formulations which contain acrylic resin, showed minimum weight loss at pigment binder ratio 1.6 (Formula A4). But series B and C formulations which contain urabrid AC100 and short oil alkyd resin, the minimum weight loss values was observed at formula B5, C5, at the same pigment binder ratio (1.8).

From the above results, it can be seen that the coatings formulated with short oil alkyd emulsion resin show high barrier properties when compared with acrylic and urabrid AC100 emulsion paint formulations. The distinguished performance of alkyd coatings can be attributed to the type of resin.

As reported by many authors, convertible coatings such as alkyds give better barrier properties than non-convertible coatings such as acrylics. Alkyd resins dry by auto-oxidation, which results in cross-linking and minimum film permeability [237, 238]. Also, it can be shown that, the increasing pigment binder ratio than the optimum concentration leads to increase porosity of the paint film and this gives the chance of water, oxygen and aggressive ions to penetrate to metal surface [239].

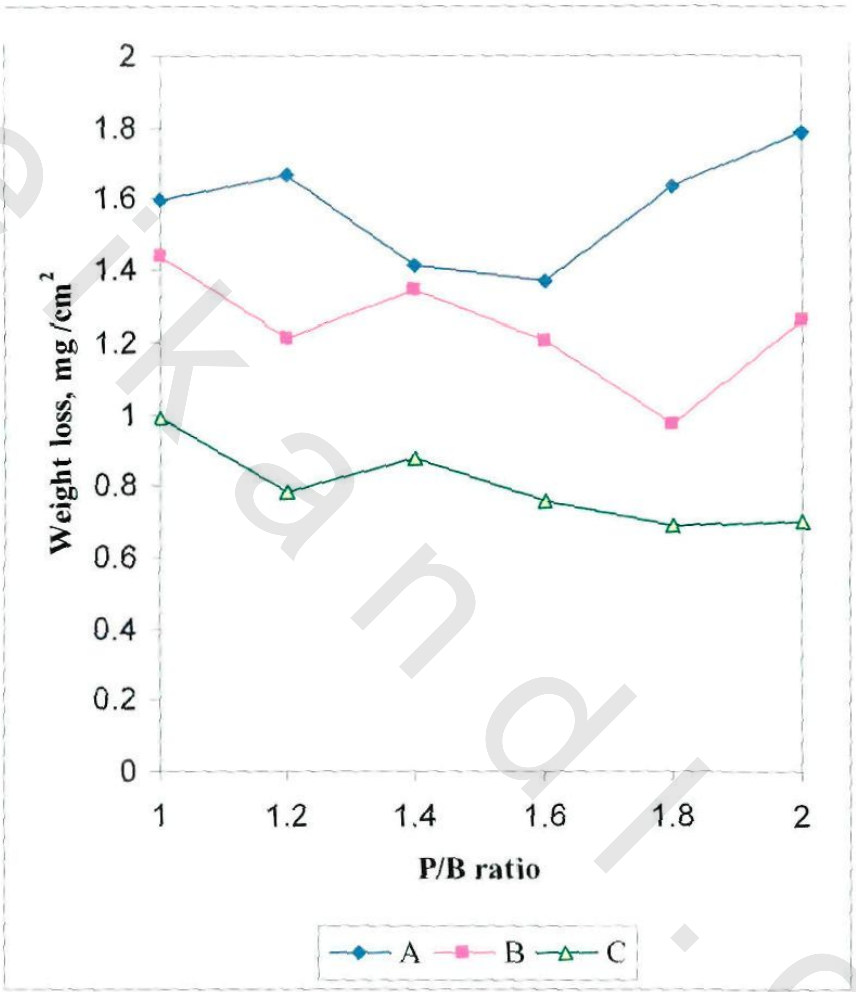


Fig. (4.12): The dependence of weight loss measurements on P/B ratios

Conclusions

- Pigment binder ratio can affect the corrosion resistance characteristics of emulsion paint coatings.
- Maximum corrosion resistance does not occur at the same value of pigment binder ratio for paint systems. Where, the value of optimum pigment binder ratio can vary depending on the nature of the binder.
- Pigment binder ratios 1.6, 1.8 and 1.8 showed maximum corrosion resistance in blank samples A, B and C, respectively.
- The best water up-take resistances were evidenced by paint samples of short oil alkyd, acrylic and urabrid AC100 respectively at their optimal pigment binder ratio.
- The best mass loss resistances were evidenced by paint samples of short oil alkyd, urabrid AC100 and acrylic respectively at their optimal pigment binder ratio.
- Increasing pigment binder ratio than optimum concentration leads to increase water up-take, blistering and degree of rusting.

4.2.2. Group II: 2-MT adduct as corrosion inhibitor

The aim of this group is to optimize the best concentration of the prepared 2-mercapto-Δ^2-thiazoline adduct as corrosion inhibitor in water-borne paint formulations based on urabrid AC100 emulsion. The prepared paints are free of anti-corrosive pigments.

Group II comprises eleven formulations based on urabrid AC100 resin. Formula B5 was selected as control, i.e. it does not contain any of the prepared sulfur adducts. Different concentrations (0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.14 and 0.15% as solid) of the emulsified 2-MT adduct were added to the blank formula.

The prepared paints are listed in Table (4.25). All concentrations of thiol adducts in the paint formulations are based on the weight of solid adducts added to 100 gm of liquid emulsion paint. Flash rusting inhibitor (ammonium benzoate) was added to all formulations in this group to prevent the corrosion phenomenon known as flash rusting, which occurs in water-borne coatings due to the direct contact of water to metal surface during drying.

All formulation characteristics such as pH, pigment binder ratio and solid content are kept constant to exclude any other variables affecting coatings performance.

Table (4.25): Emulsion paint formulation of group II

Formula No. / Composition	B5	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B1
Mill base (I)	47.1	47.1	47.1	47.1	47.1	47.1	47.1	47.1	47.1	47.1	47.1	47.
Urabrid AC100	39.54	39.54	39.54	39.54	39.54	39.54	39.54	39.54	39.54	39.54	39.54	39.5
Texanol	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Flash rust inhibitor	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Butyl glycol	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ethanol amine	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2-MT	----	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.1
Defoamer	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Biocide	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Drier	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water	8.16	8.11	8.10	8.09	8.08	8.07	8.06	8.05	8.04	8.03	8.02	8.0
Thickener	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Total weight	100	100	100	100	100	100	100	100	100	100	100	10

Formulation constants

Solid content by weight	47.6 %
pH	≥8
Pigment binder ratio	1.8

The physical, chemical and mechanical tests of all paint formulations of group (II) are listed in the following Table (4.26).

Table (4.26): Physical, chemical and mechanical properties of paint films of group II

Formula No. / Test	B5	B7	B8	B9	B10	B11	B12	B13	B14	B15	B16	B17
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	5H	5H	5H	4H	4H	4H	3H	3H	2H	2H	2H	H
Ductility	6.1	6.2	6.2	6.2	6.3	6.3	6.4	6.5	6.6	6.7	6.8	6.8
Bending	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

The above results, show that the addition of different concentrations of the emulsified 2-MT adduct has more or less, no effect before corrosion tests. All films of the investigated formulations showed high adhesion to steel panels, and excellent flexibility (bending and ductility). All coated glass samples were not affect when immersed in acid, alkali and water, this proving a distinguished chemical resistance of paint films. Results of other mechanical properties such as hardness are reasonable for all paint formulations.

The influence of emulsified 2-MT adduct on water up-take % of paint film of group (II) up to 30 days has intensively studied, the obtained results are given in Table (4.27) and plotted in Fig. (4.13).

Table (4.27): Water up-take (%) for paint films of group II

Formula No. \ Time (days)	5	10	15	20	25	30
B5	11.23	13.35	15.65	18.16	19.94	21.11
B7	9.31	12.32	13.36	15.85	17.50	17.76
B8	9.04	11.80	13.58	15.56	17.36	17.65
B9	8.49	11.48	13.44	14.75	15.52	16.50
B10	6.53	10.41	12.50	13.93	14.91	15.56
B11	5.21	9.30	11.42	12.50	14.04	14.58
B12	5.18	8.96	11.05	12.28	13.34	14.03
B13	5.28	9.52	11.53	12.58	13.57	14.39
B14	8.01	11.04	13.10	14.53	15.46	16.22
B15	8.58	11.55	13.53	15.03	16.25	17.55
B16	9.94	12.53	14.35	16.50	17.58	19.30
B17	10.55	13.11	15.05	16.93	18.25	19.75

It is clear from the above results that the minimum water up-take have been obtained with formula B12, after 30 days immersion in distilled water, while the maximum water up-take was observed at formula B17. These results are revealing that the water absorption of water-borne coatings is affected by the amount and nature of polar groups in dry paint film [141].

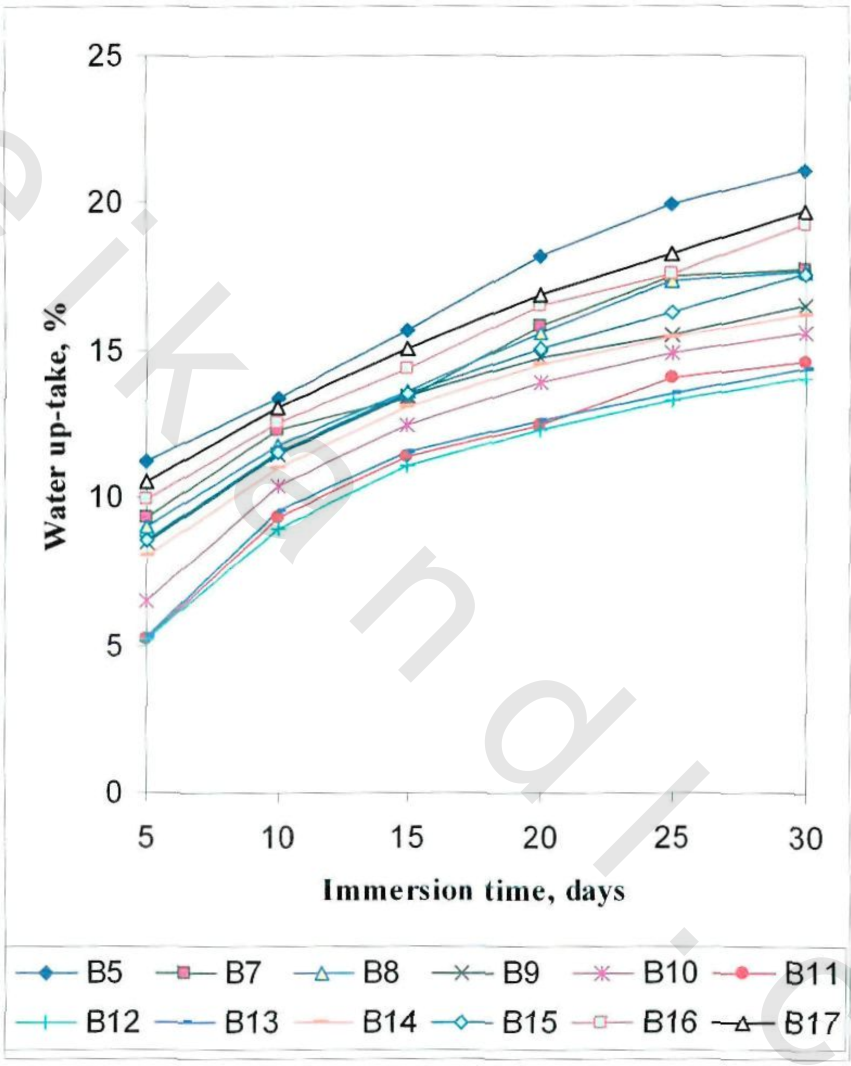


Fig. (4.13): The variation in water up-take (%) with time of immersion of group II

The results of corrosion resistance tests are given in Table (4.28). The painted metal plates of this group are detected for blistering resistance of coating films, failure around the scribe and degree of rusting of metal surface under paint films, after immersion of plates in artificial sea water for 28 days.

Table (4.28): Corrosion resistance tests for paint films of group II

Formula No. \ Test	Corrosion resistance (1)	Degree of blistering (2)	Corrosion scratch test (3)
B5	s.t.	8F	B
B7	v.s.t.	8F	B
B8	v.s.t.	6F	B
B9	v.s.t.	6F	B
B10	c	10	A
B11	c	10	A
B12	c	10	A
B13	c	10	B
B14	c	10	B
B15	v.s.t.	6F	C
B16	v.s.t.	6F	C
B17	v.s.t.	8F	C

1. ***b:*** Bright surface; ***c:*** clean; ***v.s.t***: very slight tarnishing; ***s.t.:*** slight tarnishing; ***m.t.:*** medium tarnishing; ***h.t.***: high tarnishing and ***h.t.p.:*** high tarnishing and pitting.
2. It is graded on a scale from ***10*** to ***0***, where ***10*** no blistering and ***0*** for largest blisters and frequency denoted by ***F, M, MD*** and ***D*** (few, medium, medium dense and dense) respectively.
3. ***A-E***: Corrosion just in the scratch but differs in the adhesion of the film around the scratch; ***A = Gt0, B = Gt1, C = Gt2, D = Gt3, E = Gt4.***

The above results show that the best corrosion resistance was obtained at Formula B10, B11, B12, B13 and B14. Figure (4.14) represent photos of metal plate's failure around the scribe and degree of rusting of metal surface, after 28 days immersion in sea water.

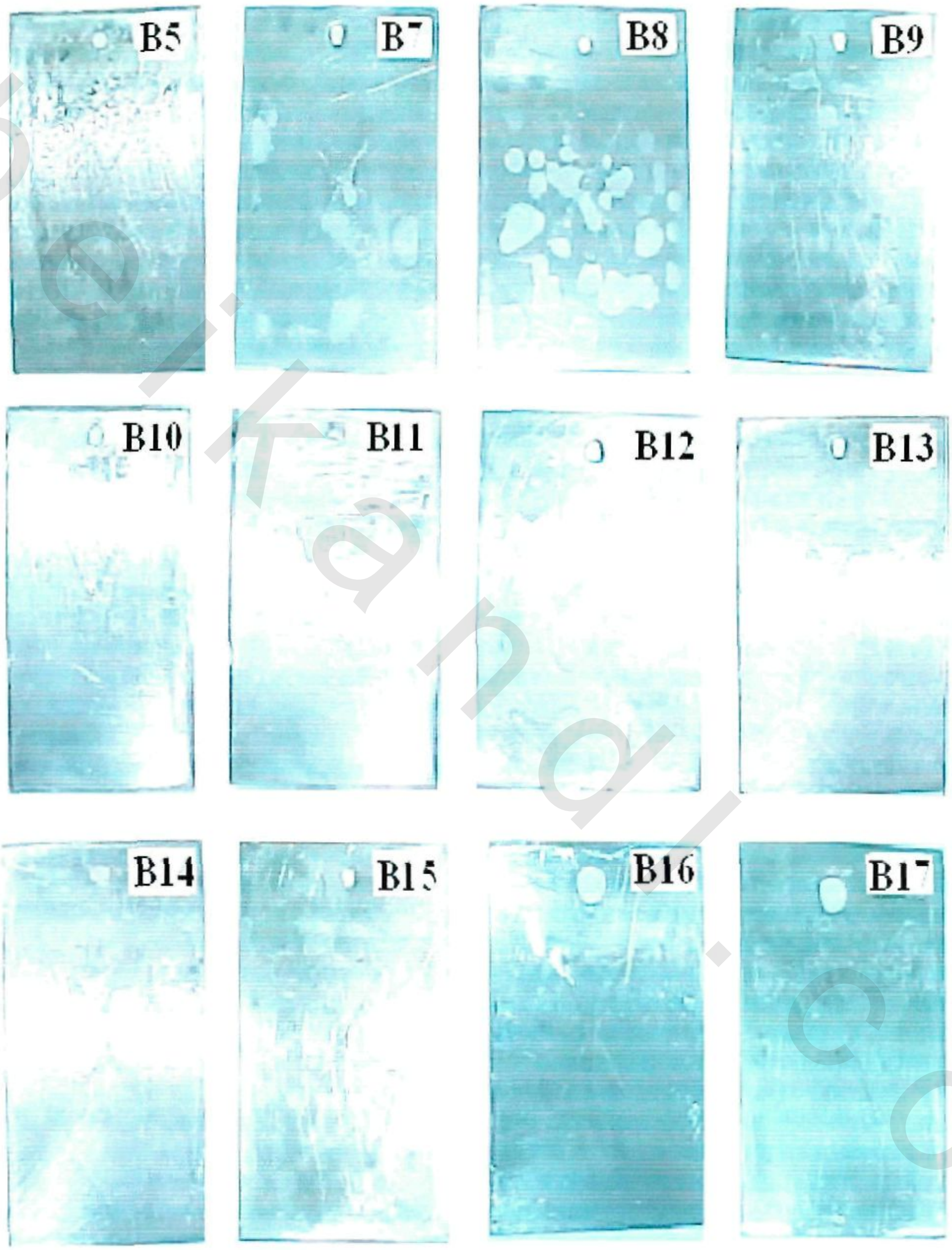


Fig. (4.14): Corrosion progress under paint films of group II after 28 days immersion in artificial sea water

The weight loss variation of paint films of this group are given in Table (4.29), and plotted in Fig. (4.15).

Table (4.29): Weight loss measurements (mg/cm^2), for steel panels under paint films of group II

Time (days) / Formula No.	10	20	30	40	50	60
B5	0.115	0.210	0.396	0.568	0.790	0.971
B7	0.104	0.192	0.306	0.415	0.523	0.626
B8	0.097	0.181	0.276	0.374	0.461	0.552
B9	0.083	0.170	0.247	0.313	0.381	0.443
B10	0.075	0.138	0.201	0.265	0.323	0.385
B11	0.051	0.085	0.130	0.181	0.240	0.315
B12	0.025	0.063	0.108	0.151	0.210	0.273
B13	0.036	0.074	0.122	0.170	0.226	0.287
B14	0.058	0.112	0.169	0.218	0.279	0.328
B15	0.071	0.125	0.184	0.244	0.310	0.363
B16	0.080	0.152	0.220	0.280	0.343	0.403
B17	0.082	0.160	0.236	0.302	0.361	0.426

The above results declare that, the addition of 2-MT adduct decreases weight loss of mild steel, i.e. it has inhibiting efficiency. The increase of the amount of 2-MT adduct enhance corrosion resistance up to 0.10 (formula B12). At higher concentrations of 2-MT adduct than that concentration, corrosion starts to appear again in the scratch with some loss of adhesion of the paint films to the metal surface. The slightly higher values of weight loss observed in paint formula B16, B17 may be explained as follows:

The emulsified adduct at optimum concentration may form an adsorbed mono-layer film on the metal surface and the adduct molecules may direct themselves to be adsorbed on the metal surface via the lone pair of electrons on the sulfur atom of the (-SH) group and oxygen atom of the hydroxyl group; so the adhesion of the paint films may be improved. Moreover the hydrocarbon tails of the oil, which is originally hydrophobic in character, may find the chance to orient themselves away from the metal interface toward the coat bulk, thus further protection is provided by the formation of originally hydrophobic network, which excludes water and aggressive ions from the metal surface; Fig. (4.16a) may explain the proposed mechanism. On the other hand the excess amounts of the emulsified adduct may lead to random distribution of the excess amount in the bulk of emulsion paint film. These unarranged polar molecules may act to drive more water molecules from the surrounding medium through the hydrophilic groups; consequently, they may oppose the action of protection and produce emulsion paint films of less protective properties on prolonged exposure, Fig. (4.16b) may illustrate this phenomenon [240].

4.2.2.1. Corrosion inhibition efficiency

It is stimulating to study the inhibition efficiency of different concentrations of the 2-MT adduct in urabrid AC100 emulsion binder. The percentage of inhibition efficiency can be measured according to the following equation:

$$I(\%) = \{(Wo - Wi) / Wo\} \times 100$$

Where, Wo is the weight loss values for metal of paint films without adduct, and Wi is the weight loss values in the presence of 2-MT adduct. Table (4.30) and Fig. (4.17) represent the inhibition efficiency (IE) of different concentrations (0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11 , 0.12 , 0.13 , 0.14 and 0.15) of the adduct as corrosion inhibitor in urabrid AC100 paint films after 60 days immersion in artificial sea water.

Table (4.30): Corrosion inhibition efficiency of different concentrations of (2-MT) adduct

2-MT conc.	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15
IE, %	35.53	43.15	54.38	60.35	67.56	71.88	70.44	66.22	62.62	58.49	56.12

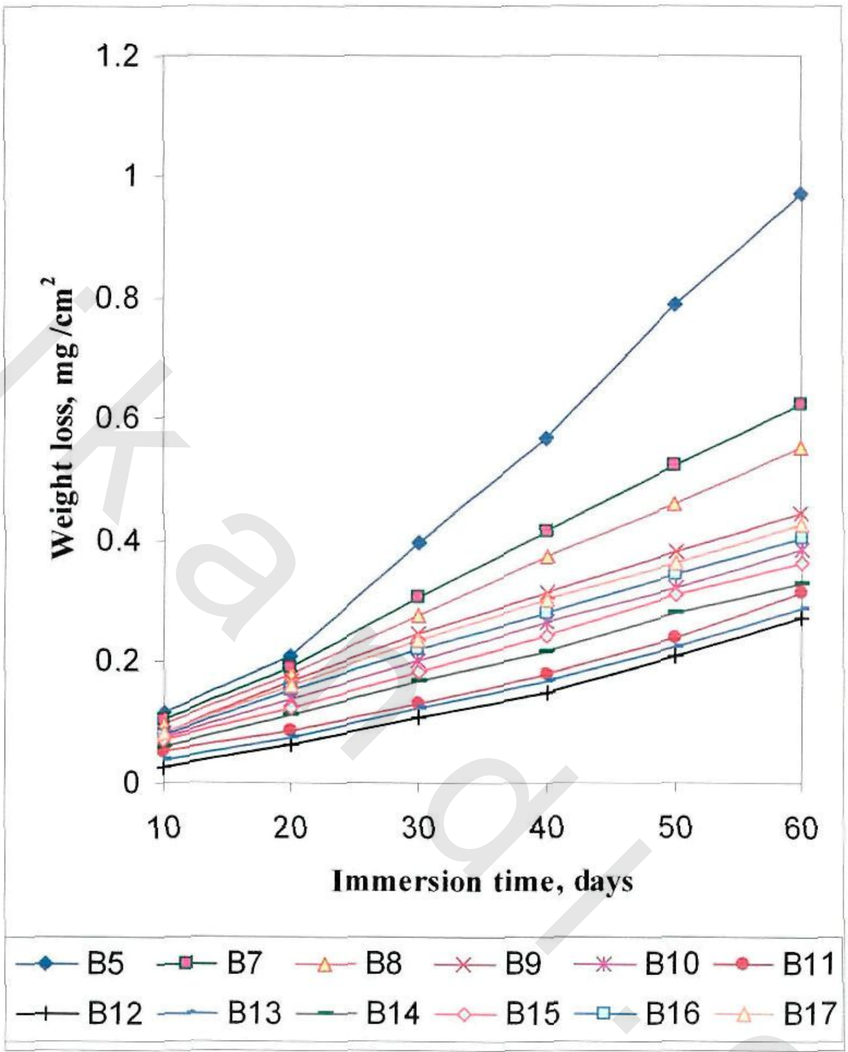


Fig. (4.15): The dependence of weight loss on the immersion time for paint formulations of group II

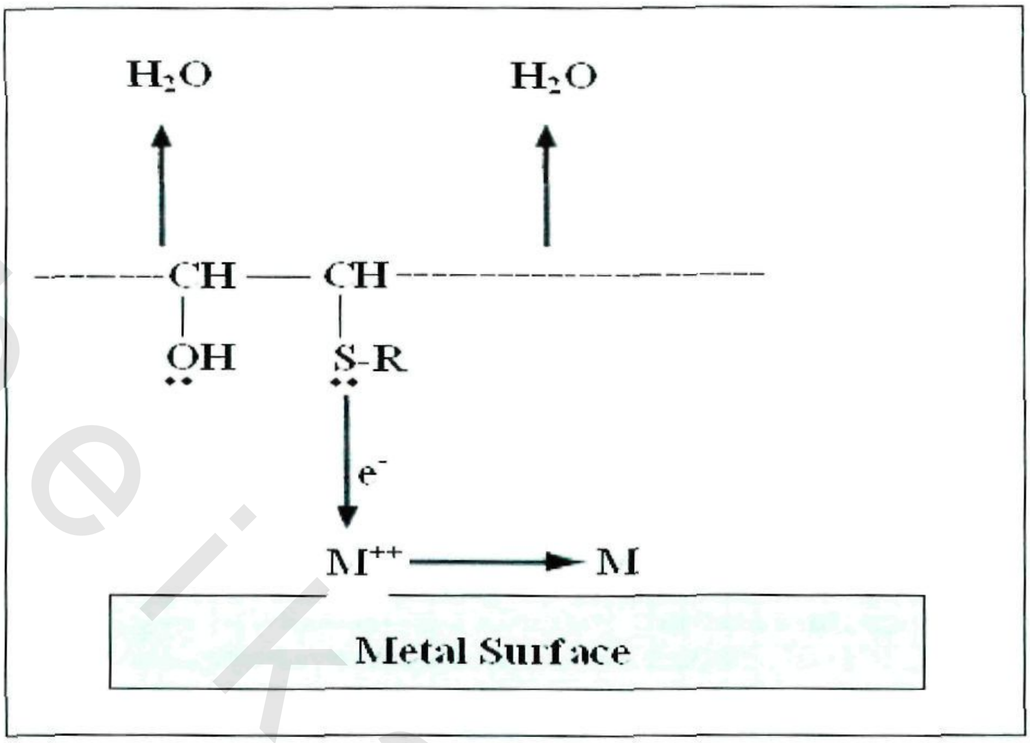


Fig. (4.16a): Mechanism of corrosion inhibition at optimum concentration of inhibitor

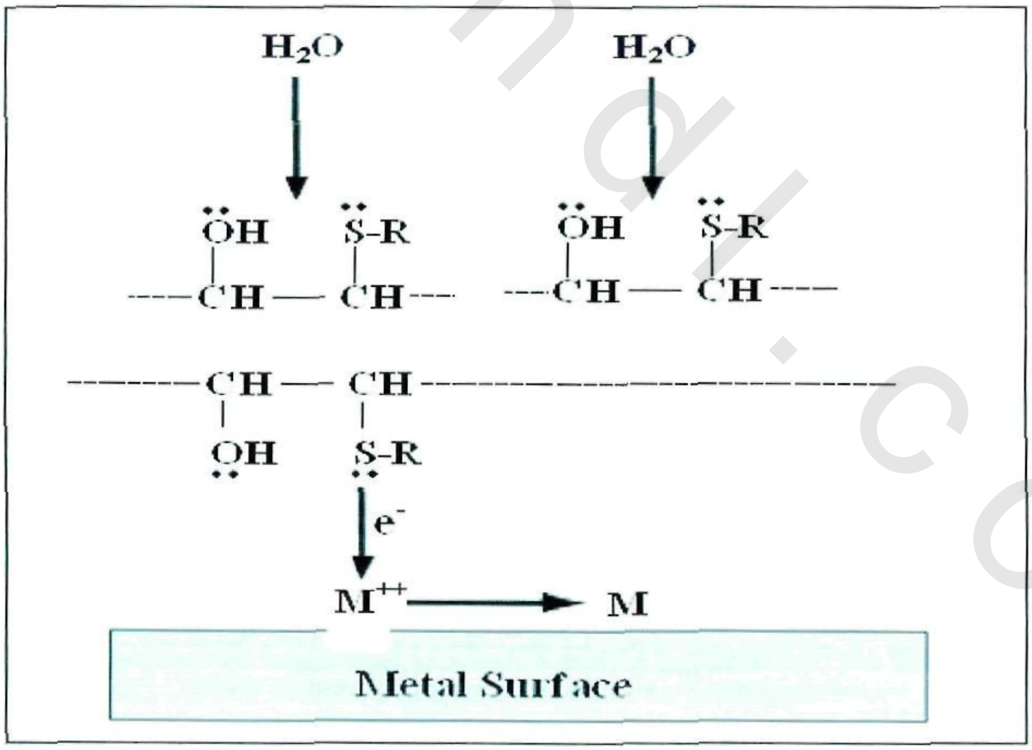


Fig. (4.16b): Mechanism of corrosion inhibition at higher concentration of inhibitor

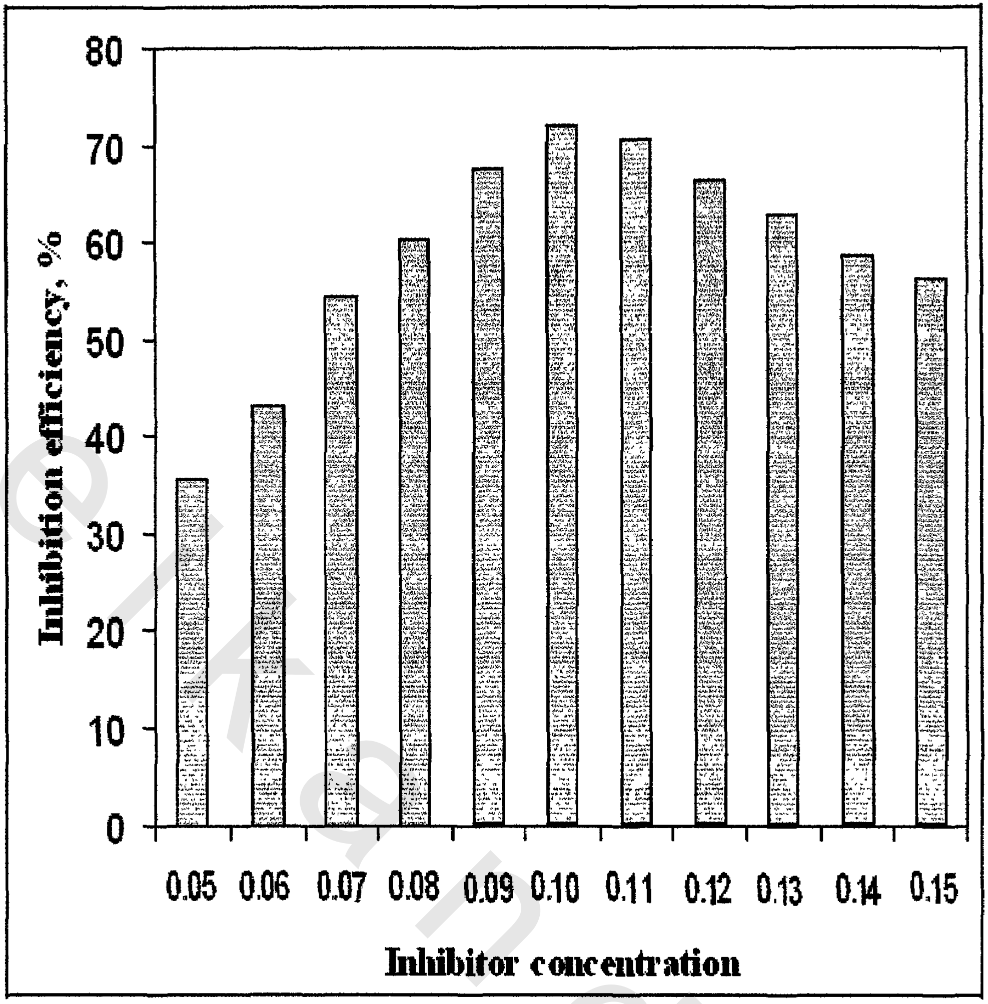


Fig. (4.17): Variation of 2-MT concentrations vs. corrosion inhibition efficiency

Conclusion

- Steel panels could be protected by addition of small concentrations of the emulsified inhibitor to emulsion paint formulation free of anti-corrosive pigments, i.e. 2-MT adduct can be used as corrosion inhibitor.
- The optimum range concentration (0.09, 0.10 and0.11 gm) of 2-MT adduct per 100 gm of urabrid AC100 emulsion paint, may cause the most protective corrosion inhibition.
- Concentration more than optimum range of 2-MT adduct per 100 gm of urabrid AC100 emulsion paint may oppose the action of protection.

4.2.3. Group III: Optimization of the best sulfur adduct as corrosion inhibitor

The aim of this group is to arrange the prepared emulsified adducts of 2-MT, 2-MBT, 2-MMT, and 3-MMT according to their efficiencies as corrosion inhibitor for mild steel. Four formulations based on urabrid AC100 emulsion resin containing fixed concentration 0.10% as solid adduct.

This group comprises four paint formulations in addition to blank formula as shown in Table (4.31). All paint formulations of this group do not contain any type of anti-corrosive pigments. The paint formulations (B12, B18, B19 and B20) contain fixed concentration 0.10% (which was found to be the optimum concentration as shown in the previous paint formulations) of the prepared sulfur adducts (2-MT, 2-MBT, 2-MMT and 3-MMT) respectively. All formulation characteristics are kept constant to clarify the inhibitive effect of the prepared inhibitors.

Table (4.31): Emulsion paint formulation of group III

Composition \ Formula No.	B5	B12	B18	B19	B20
Mill base (I)	47.1	47.1	47.1	47.1	47.1
Urabrid AC100	39.54	39.54	39.54	39.54	39.54
Texanol	0.5	0.5	0.5	0.5	0.5
Flash rust inhibitor	2.0	2.0	2.0	2.0	2.0
Butyl glycol	1.0	1.0	1.0	1.0	1.0
Ethanol amine	1.0	1.0	1.0	1.0	1.0
2-MT	----	0.10	----	----	----
2-MBT	----	----	0.10	----	----
2-MMT	----	----	----	0.10	----
3-MMT	----	----	----	----	0.10
Anti-foaming agent	0.2	0.2	0.2	0.2	0.2
Biocide	0.1	0.1	0.1	0.1	0.1
Drier	0.2	0.2	0.2	0.2	0.2
Water	8.16	8.06	8.06	8.06	8.06
Thickener	0.2	0.2	0.2	0.2	0.2
Total weight	100	100	100	100	100

Formulation constants

Solid content by weight	47.6 %
pH	≥8
Pigment binder ratio	1.8

The physical, chemical and mechanical properties of paint films of this group are given in Table (4.32).

Table (4.32): Physical, chemical and mechanical properties of paint films of group III

Tests \ Formula No.	B5	B12	B18	B19	B20
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	5H	3H	4H	3H	3H
Ductility	6.1	6.3	6.2	6.3	6.4
Bending	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.

It is clear from the above Table that the addition of the emulsified thiol adducts has more or less no effect on the investigated properties. All films of the investigated formulations showed excellent adhesion on steel panels, which is the basic requirement for high corrosion inhibition performance. The results of other properties such as hardness, ductility and bending are reasonable and nearly equal to the blank. On the other hand, all paint films of this group were not affected by acid, alkali and water, and this provided a distinguished chemical resistance of the paint films. This means that the addition of the prepared adduct has more or less no effect on physical, chemical and mechanical properties the paint films.

The influence of the emulsified thiol adducts on water up-take % of paint films of group (III) up to 30 days was intensively studied. The obtained results are collected in Table (4.33) and represented graphically in Fig. (4.18).

Table (4.33): Water up-take (%) for paint films of group III

Time (days) / Formula No.	5	10	15	20	25	30
B5	11.23	13.35	15.65	18.16	19.94	21.11
B12	5.18	8.96	11.05	12.28	13.34	14.03
B18	4.13	7.90	9.87	11.50	12.83	13.15
B19	3.16	5.84	8.15	10.35	11.12	12.00
B20	2.21	4.52	6.90	8.61	10.05	11.17

From the above results, it is clear that the paint formula B20, which contain 3-MMT adduct, has the lowest water up-take value. The water up-take of the emulsified prepared adducts can be arranged in the following descending order: 3-MMT > 2-MMT > 2-MBT > 2-MT

The corrosion tests of the samples were evaluated as a function of immersion time. Blistering of the paint films, corrosion under the paint films and rating of failure at the scribe were followed up at the end of immersion time (28 days). The results of this group are given in Table (4.34) and represented graphically in Fig. (4.19).

Table (4.34): Corrosion resistance tests for paint films of group III

Formula No. / Test	B5	B12	B18	B19	B20
Corrosion resistance (1)	s.t	c	b	b	b
Degree of blistering (2)	8F	10	10	10	10
Corrosion scratch test (3)	B	A	A	A	A

1. ***b:*** Bright surface; ***c:*** clean; ***v.s.t***: very slight tarnishing; ***s.t.:*** slight tarnishing; ***m.t.:*** medium tarnishing; ***h.t.***: high tarnishing and ***h.t.p.:*** high tarnishing and pitting.
2. It is graded on a scale from ***10*** to ***0***, where ***10*** no blistering and ***0*** for largest blisters and frequency denoted by ***F, M, MD*** and ***D*** (few, medium, medium dense and dense) respectively.
3. ***A-E***: Corrosion just in the scratch but differs in the adhesion of the film around the scratch; ***A = Gt0, B = Gt1, C = Gt2, D = Gt3, E = Gt4.***

As shown in the above Table, the blank formula B5 (which does not contain inhibitor) shows slight tarnishing corrosion resistance. But other formulations which contain inhibitor have best corrosion inhibition efficiency, where a bright clean surface was investigated under the paint films.

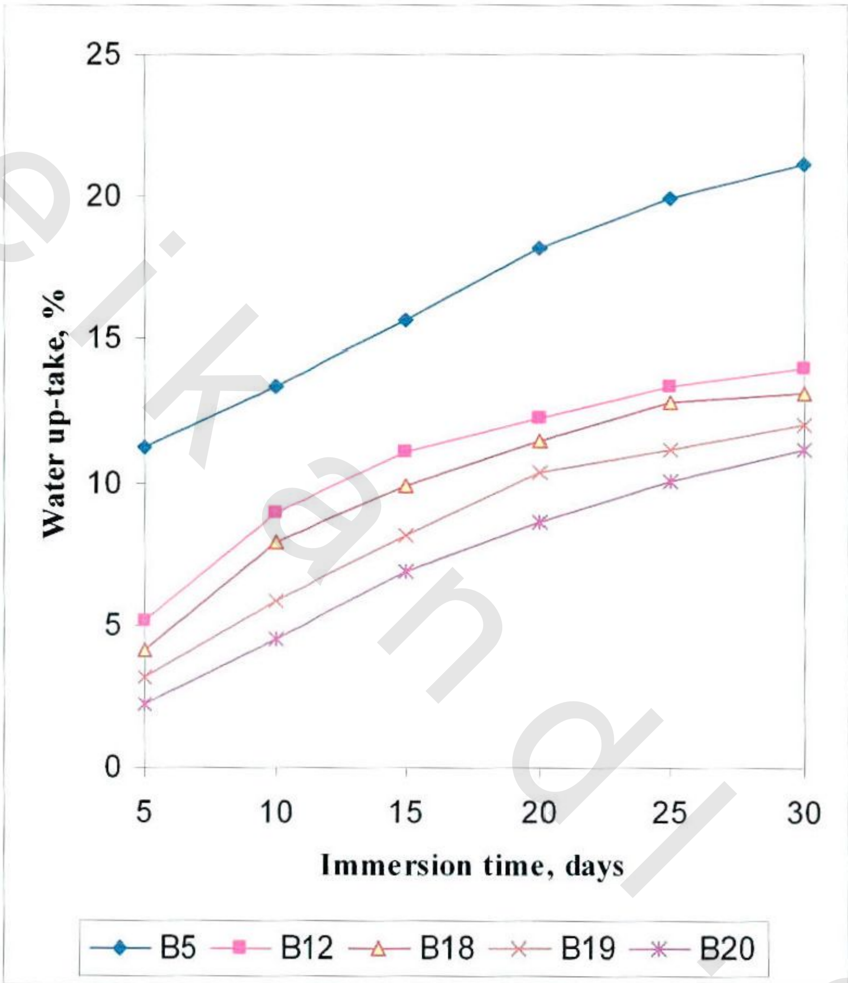


Fig. (4.18): The variation in water up-take (%) with time of immersion of group III

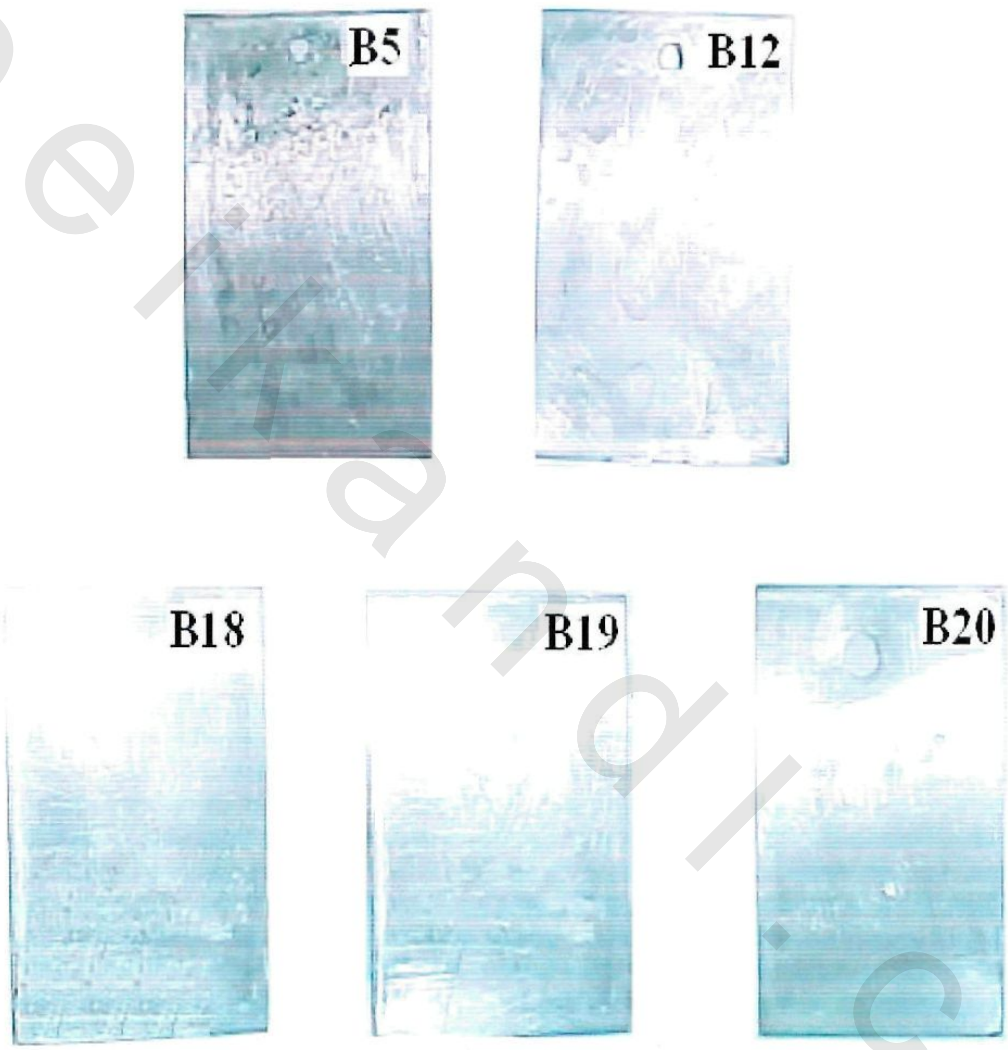


Fig. (4.19): Corrosion progress under paint films of group III after 28 days immersion in artificial sea water

Weight loss measurements are given in the Table (4.35) and plotted in Fig. (4.21).

Table (4.35): Weight loss measurements (mg/cm^2), for steel panels under paint films of group III

Formula No. \ Time (days)	10	20	30	40	50	60
B5	0.115	0.210	0.396	0.568	0.790	0.971
B12	0.025	0.063	0.108	0.151	0.210	0.273
B18	0.023	0.056	0.095	0.140	0.196	0.260
B19	0.018	0.043	0.081	0.123	0.177	0.244
B20	0.016	0.039	0.072	0.118	0.164	0.241

Table (4.35) and Figure (4.20) reveals that the minimum weight loss values (0.241 mg/cm^2) has been observed with the steel panel coated by formula B20, which contains 3-MMT adduct all over the immersion period (60 days).

A comparative study of corrosion inhibitors performance of the prepared emulsified adducts (2-MT, 2-MBT, 2-MMT, and 3-MMT) after 60 days immersion in sea water according to their inhibition efficiencies is shown in Table (4.36) and represented in Fig. (4.21).

As can be seen, 3-MMT adduct revealed superior corrosion inhibition efficiency (about 75.18%), while in case of 2-MMT adduct (about 74.87%) corrosion inhibition efficiency was attained. With respect to 2-MBT and 2-MT adducts the inhibition efficiency were about 73.22 and 71.88% respectively.

Table (4.36): Corrosion inhibition efficiency

Adduct type	**2-MT**	**2-MBT**	**2-MMT**	**3-MMT**
Efficiency, (%)	71.88	73.22	74.87	75.18

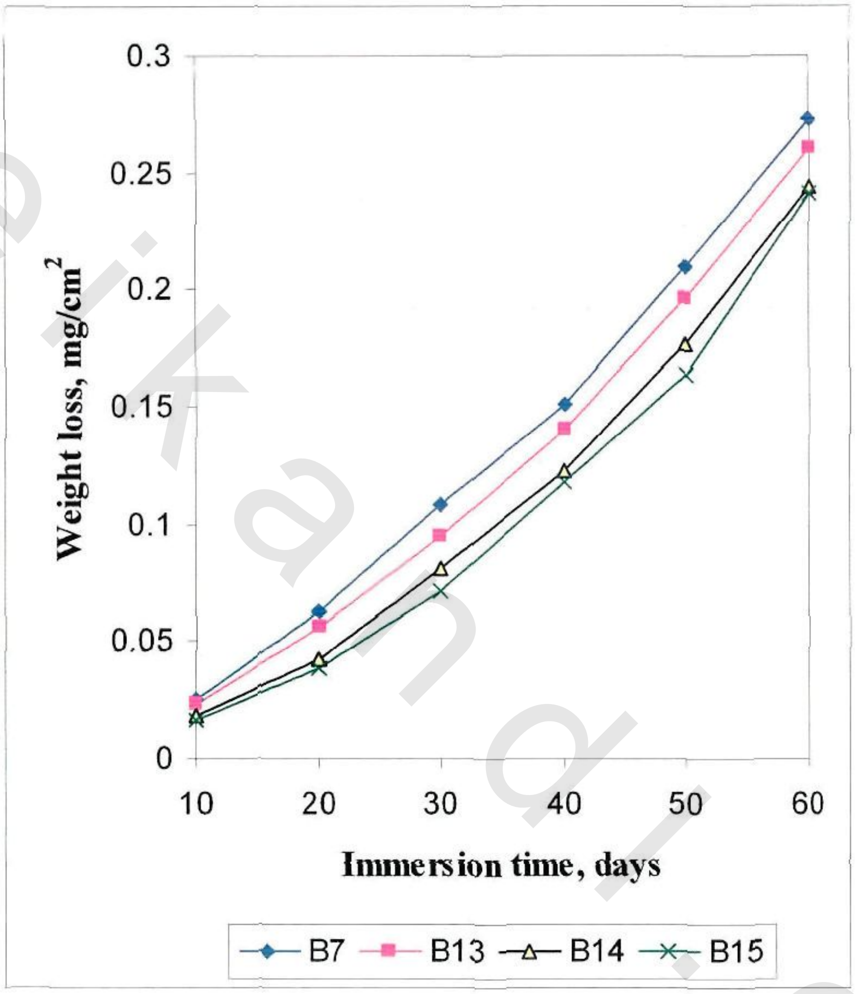


Fig. (4.20): The dependence of weight loss on the immersion time for paint formulations of group III

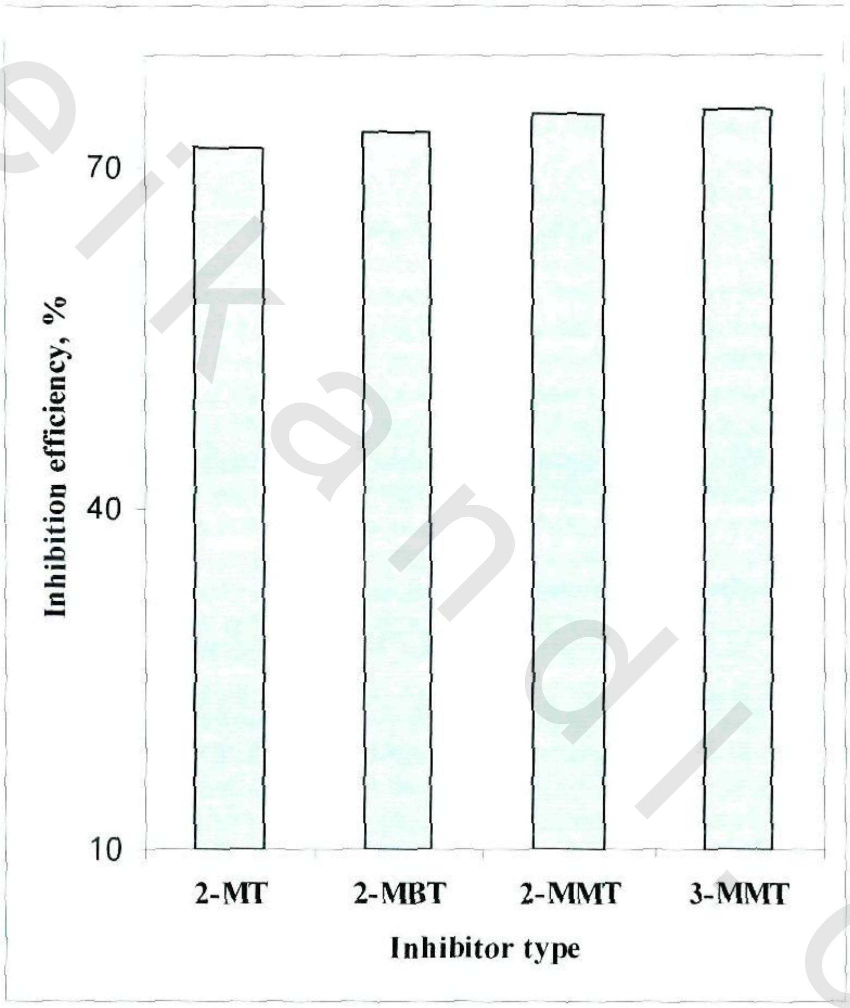


Fig. (4.21): Adduct inhibitors vs. corrosion inhibition efficiency

The above results may lead to conclusion that the prepared adducts can be adsorbed on the mild steel surface and displace water molecules on the surface to form a compact barrier thin film. This film may make co-ordination bond between inhibitors and iron surface causes higher inhibition efficiency. The ability of the molecule to chemisorb on the steel surface is depend on the electron density around the adsorption center of inhibitor [241, 242] .

The obtained results indicate that the inhibition effeciency of the prepared adducts at the chosen concentration increases in the order: 2-MT < 2-MBT < 2-MMT < 3-MMT adducts. But the difference in inhibition efficiency between the highest and lowest efficiency is low (3.3 %).

Conclusions

- The prepared inhibitors protect metal surface from corrosion.
- The emulsified 3-MMT adduct is the most efficient inhibitor, which gave highest corrosion protection of the steel surface.
- The efficiency of the emulsified prepared adducts as corrosion inhibitors can be arranged in the following descending order:

  3-MMT > 2-MMT > 2-MBT > 2-MT

4.2.4. Group IV: Evaluation of different binder systems

In the latter group, the assessment of the behavior of the prepared emulsified adducts (which are used as organic corrosion inhibitors) showed a superior performance of 3-MMT adduct over other adducts within the same concentration range using water-borne urabrid AC100 paint formulations. So, it is interesting to study the effect of resin type on the corrosion resistance of anti-corrosive coatings using 3-MMT adduct as a sole corrosion inhibitor.

In this group, three types of emulsion binders (acrylic, short oil alkyd and urabrid AC100 emulsion resins) were used. The emulsified 3-MMT adduct was added at constant concentration 0.1% for the three types of emulsion binders. The paint formulations are given in Table (4.37).

All formulation characteristics were kept constant, while pigment binder ratios of all binder types were adjusted at their maximum function barrier (1.6 for acrylic and 1.8 for short oil alkyd and urabrid AC100 emulsion resins).

Table (4.37): Emulsion paint formulation of group IV

Composition \ Formula No.	B5	B20	A4	A7	C5	C7
Mill base (I)	47.1	47.1	41.9	41.9	47.1	47.1
Urabrid AC100	39.54	39.54	----	----	----	----
Acrylic emulsion	----	----	30.91	30.91	----	----
Alkyd emulsion	----	----	----	----	37.8	37.8
Binder as solid	17	17	17	17	17	17
Texanol	0.5	0.5	1.0	1.0	0.6	0.6
Flash rust inhibitor	2.0	2.0	3.2	3.2	2.2	2.2
Butyl glycol	1.0	1.0	1.7	1.7	1.0	1.0
Ethanol amine	1.0	1.0	1.5	1.5	1.0	1.0
3-MMT	----	0.10	----	0.10	----	0.10
Anti-foaming agent	0.2	0.2	0.3	0.3	0.2	0.2
Biocide	0.1	0.1	0.2	0.2	0.1	0.1
Drier	0.2	0.2	----	----	0.2	0.2
Water	8.16	8.06	18.79	18.69	9.6	9.50
Thickener	0.2	0.2	0.5	0.5	0.2	0.2
Total weight	100	100	100	100	100	100
Solid content by wt, %	47.6	47.6	44.2	44.2	47.6	47.6
Pigment binder ratio	1.8	1.8	1.6	1.6	1.8	1.8

Formulation constants

pH ≥ 8

The physical, chemical and mechanical properties of emulsion paint formulations of group IV are represented in Table (4.38). It is noticed from this Table that the physical, chemical and mechanical properties of the three types of resins do not affected by the addition of 3-MMT adduct. Satisfactory chemical test results were obtained for the three types of resin paint formulations.

Table (4.38): Physical, chemical and mechanical properties of paint films of group IV

Test \ Formula No.	B5	B20	A4	A7	C5	C7
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness	5H	3H	3H	2H	5H	5H
Ductility	6.1	6.4	6.9	6.9	6.1	6.1
Bending	Pass	Pass	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Alkali resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.
Water resistance	v.g.	v.g.	v.g.	v.g.	v.g.	v.g.

Water up-take measurements for paint formulations of this group were summarized in Table (4.39), while Fig. (4.22) show the relationship between water up-take % of immersed paint films and immersion time up to 30 days.

Table (4.39): Water up-take (%) for paint films of group IV

Formula No. \ Time (days)	5	10	15	20	25	30
B5	11.23	13.35	15.65	18.16	19.94	21.11
B20	2.21	4.52	6.90	8.61	10.05	11.17
A4	5.84	8.82	11.06	13.21	15.53	16.23
A7	2.23	4.25	5.65	7.27	8.96	10.12
C5	3.87	5.33	8.60	10.73	12.62	13.41
C7	1.24	3.54	5.15	6.43	8.48	9.75

The above Table shows that the short oil alkyd paint formula has the minimum water up-take values compared with the corresponding paint films based on acrylic and urabrid AC100 resins. Generally, the protective properties of the three used binders can be arranged as follow:

Short oil alkyd emulsion > Acrylic emulsion > Urabrid AC100 emulsion

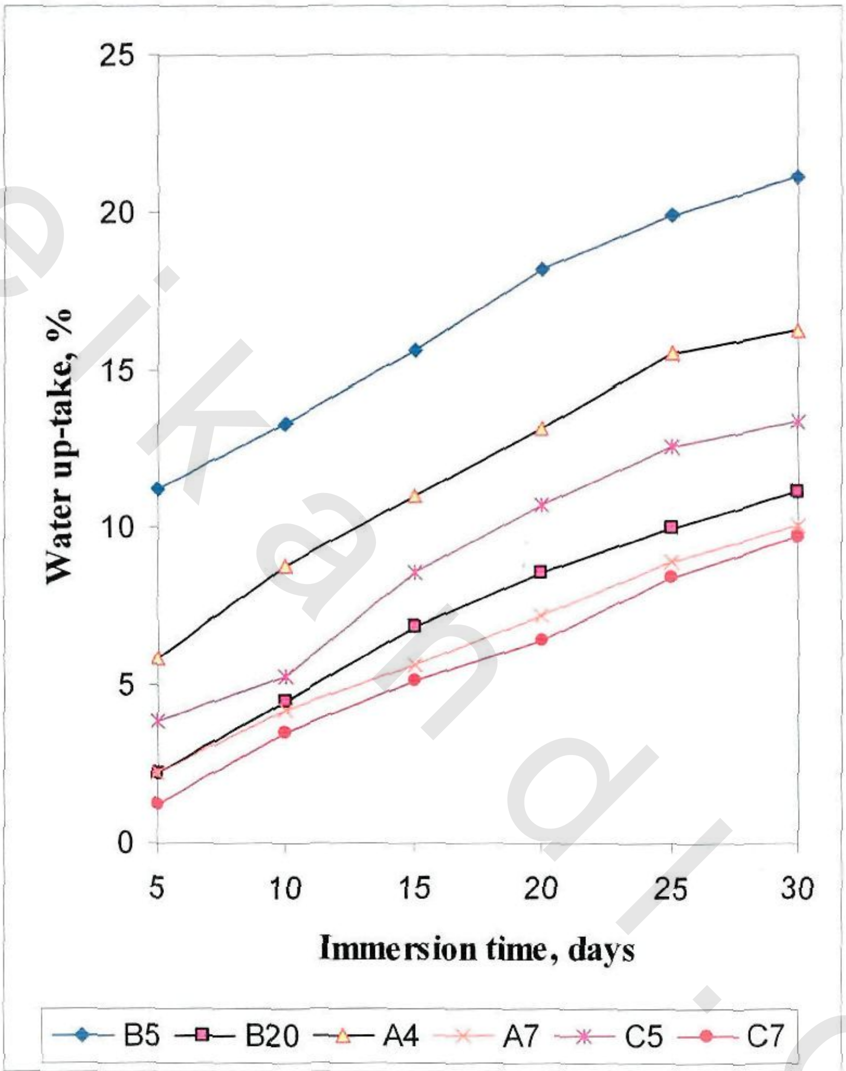


Fig. (4.22): The variation in water up-take (%) with time of immersion of group IV

Corrosion resistance results of the immersed films, for 28 days, are given in Table (4.40), while Fig. (4.23) show photos of the scribed coated steel panels at the end of test period.

Table (4.40): Corrosion resistance tests for paint films of group IV

Test \ Formula No.	B5	B20	A4	A7	C5	C7
Corrosion resistance (1)	s.t	b	c	b	b	b
Degree of blistering (2)	8F	10	10	10	10	10
Corrosion scratch test (3)	B	A	A	A	A	A

1. ***b:*** Bright surface; ***c:*** clean; ***v.s.t***: very slight tarnishing; ***s.t.:*** slight tarnishing; ***m.t.:*** medium tarnishing; ***h.t.***: high tarnishing and ***h.t.p.:*** high tarnishing and pitting.
2. It is graded on a scale from ***10*** to ***0***, where ***10*** no blistering and ***0*** for largest blisters and frequency denoted by ***F, M, MD*** and ***D*** (few, medium, medium dense and dense) respectively.
3. ***A-E***: Corrosion just in the scratch but differs in the adhesion of the film around the scratch; ***A = Gt0, B = Gt1, C = Gt2, D = Gt3, E = Gt4.***

The above results show a significant superior performance of the used binders where no sings of blisters over the paint film surfaces and no signs of corrosion have been observed under the paint films.

Concerning weight loss measurements, it was evident that the weight loss results for 60 days immersion of coated steel panels in artificial sea water were consistent with the latter observations of corrosion resistance experiments, as given in Table (4.41) and illustrated in Fig. (4.24).

Table (4.41): Weight loss measurements (mg/cm^2), for steel panels under paint films of group IV

Formula No. \ Time (days)	10	20	30	40	50	60
B5	0.115	0.210	0.396	0.568	0.790	0.971
B20	0.016	0.039	0.072	0.118	0.164	0.241
A4	0.349	0.516	0.702	0.911	1.122	1.367
A7	0.052	0.096	0.143	0.216	0.282	0.340
C5	0.105	0.162	0.301	0.466	0.584	0.688
C7	0.013	0.022	0.049	0.084	0.130	0.168

As reported in the above Table, sample C7 showed the lowest corrosion rate (0.168 mg/cm^2) under the paint film of short oil alkyd resin. While the sample A7 show high corrosion rate (0.340 mg/cm^2) under the paint film of acrylic resin.

A comparative study of corrosion inhibition efficiency of 3-MMT emulsion adduct incorporated in different resins in the previously investigated emulsion resins is shown in Fig. (4.25). As can be seen, short oil alkyd emulsion resin revealed superior corrosion inhibition efficiency (about 75.58%), while in case of urabrid AC100 emulsion resin (about 75.18%) corrosion inhibition efficiency was attained; but acrylic emulsion resin showed the lowest inhibition efficiency was obtained (about 75.13%).

Generally; the protective properties of the three used binders against corrosion can be arranged in the following order:

Short oil alkyd emulsion > Urabrid AC100 emulsion > Acrylic emulsion.

Fig. (4.23): Corrosion progress under paint films of group IV after 28 days immersion in artificial sea water

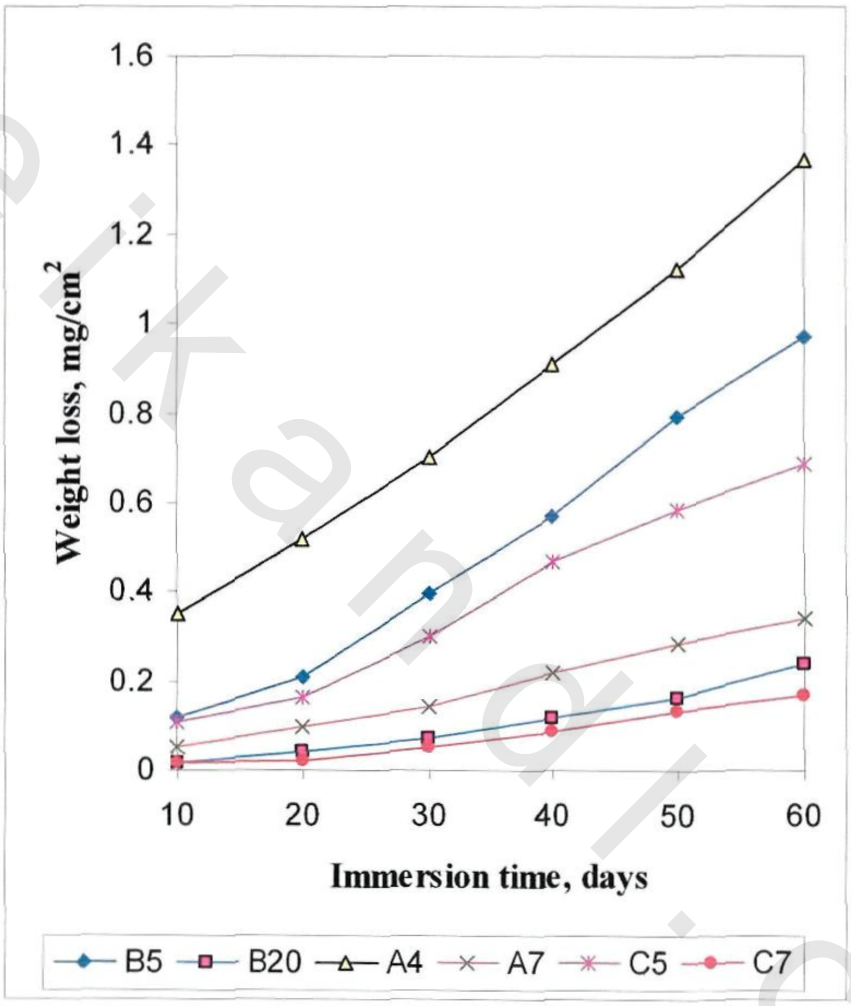


Fig. (4.24): The dependence of weight loss on the immersion time for paint formulations of group IV

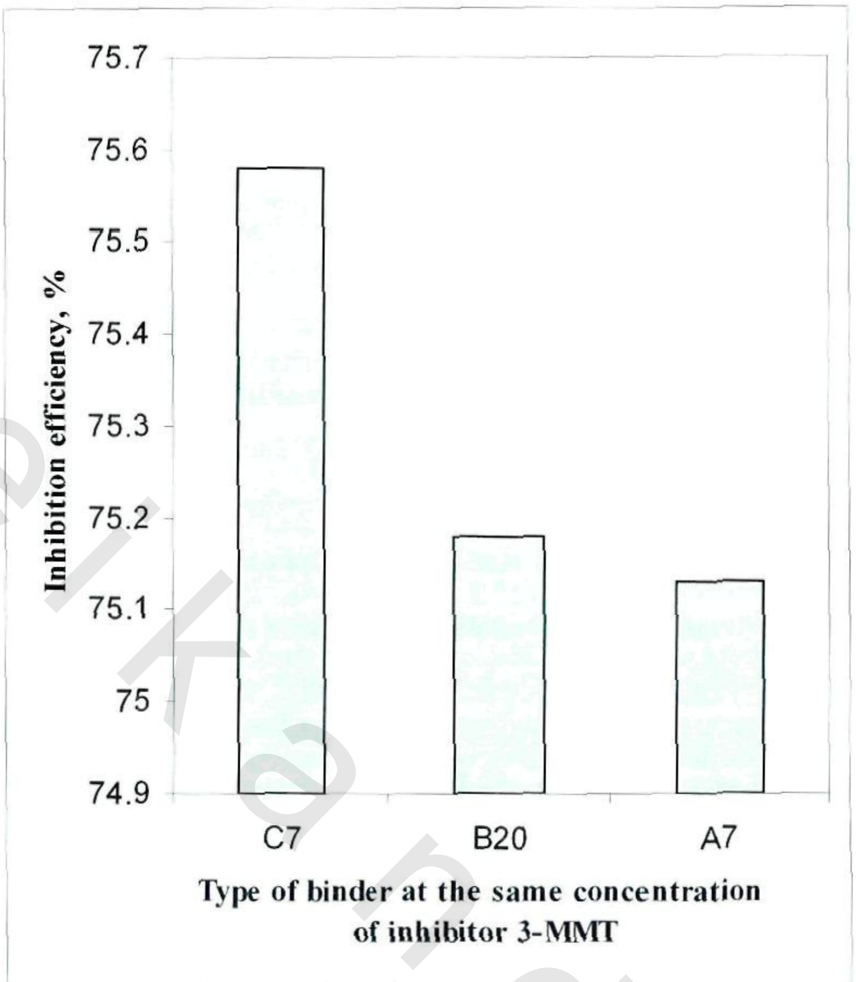


Fig. (4.25): Effect of binder type vs. corrosion inhibition efficiency

Conclusion

- The (3-MMT) adduct has confirmed a good compatibility with short oil alkyd, acrylic and urabrid AC100 emulsion resins.
- The protective properties of paints containing short oil alkyd emulsion polymer as binder are better than those containing acrylic and urabrid AC100 emulsion resins.

4.2.5. Group V: Urabrid AC100 paint formulations containing different types of pigments

It is interesting to compare the corrosion inhibition performance of urabrid AC100 coatings formulated containing (3-MMT) adduct, with those coating containing the most commonly used zinc chromate as an inhibitive pigment and zinc phosphate as barrier/inhibitive pigment. It is well known that chromate ions of zinc chromate control the corrosion by direct interaction with metal substrate or further oxidation of previously formed oxide/hydroxide layer. Zinc phosphate hydrolyzes to form zinc hydroxide and secondary phosphate ions, phosphate ions form basic iron (III) phosphate as a complex on the iron surface. Although chromate pigments are good inhibitive pigments, due to their toxic effect their replacement with other pigments is necessary.

Mill base compositions of zinc phosphate and zinc chromate pigments are represented in Table (4.42).

Table (4.42): Composition of mill base II & mill base III

Component	Mill base (II), wt	Mill base (III), wt
Titanium dioxide (Rutile)	8.20	8.20
Talc	11.20	11.20
Zinc phosphate	45.6	-----
Zinc chromate	-----	45.6
Dispersing /wetting agent	1.53	1.53
Anti-foaming agent	0.40	0.40
Ethanol amine	1.0	1.0
Water	32.07	32.07
Total weight	100	100

The emulsion paint formulations of group (V) are listed in Table (4.43). It can be seen from this Table that no flash rust inhibitors were added to zinc phosphate and zinc chromate paint formulations, where these pigments have remarked flash rust inhibition properties.

Table (4.43): Emulsion paint formulation of group V

Composition \ Formula No.	B5	B20	B21	B22
Urabrid AC100	39.54	39.54	39.54	39.54
Mill base (I)	47.1	47.1	----	----
Mill base (II)	----	----	47.1	----
Mill base (III)	----	----	----	47.1
Texanol	0.5	0.5	0.5	0.5
Flash rust inhibitor	2.0	2.0	----	----
Butyl glycol	1.0	1.0	1.0	1.0
Ethanol amine	1.0	1.0	1.0	1.0
3-MMT	----	0.1	----	----
Anti-foaming agent	0.2	0.2	0.2	0.2
Biocide	0.1	0.1	0.1	0.1
Drier	0.2	0.2	0.2	0.2
Water	8.16	8.06	8.16	8.16
Thickener	0.2	0.2	0.2	0.2
Total weight	100	100	100	100

Formulation constants

Solid content by weight 47.6 %
pH ≥ 8
Pigment binder ratio 1.8

Mechanical results of the investigated samples, as shown in Table (4.44), revealed that no adverse effect due to addition of zinc phosphate and zinc chromate. Moreover, a slight increase in hardness and hence lower ductility characteristics obtained for paint formulations containing zinc phosphate. On the other hand, chemical resistance results show no remarkable effects on the paint films, except for those containing zinc chromate pigment, where it fading in its yellow color without any damage of the film matrix has been occurred during exposure to acid and alkali solutions. This may be attributed to sensitivity of chromate pigment toward chemicals.

Table (4.44): Physical, chemical and mechanical properties of paint films of group V

Test \ Formula No.	B5	B20	B21	B22
Adhesion	Gt0	Gt0	Gt0	Gt0
Hardness	5H	3H	3H	2H
Ductility	6.1	6.4	6.5	6.9
Bending	Pass	Pass	Pass	Pass
Acid resistance	v.g.	v.g.	v.g.	F.c.*
Alkali resistance	v.g.	v.g.	good	F.c.*
Water resistance	v.g.	v.g.	v.g.	v.g.

****F.c.*: *Fading of color without damage of the paint***

Water up-take results are outlined in Table (4.45) and plotted in Fig. (4.26)

Table (4.45): Water up-take (%) for paint films of group V

Formula No. \ Time (days)	5	10	15	20	25	30
B5	11.23	13.35	15.65	18.16	19.94	21.11
B20	2.21	4.52	6.90	8.61	10.05	11.17
B21	6.86	9.94	12.41	13.60	14.53	15.33
B22	8.74	12.36	14.18	15.64	17.82	18.87

The above results show a considerable decrease in water up-take values of the paint films containing zinc phosphate (B21) and zinc chromate (B22) comparable with the blank paint formula containing titanium dioxide and talc (B5). This phenomenon may be attributed to the positive barrier effect of these pigments.

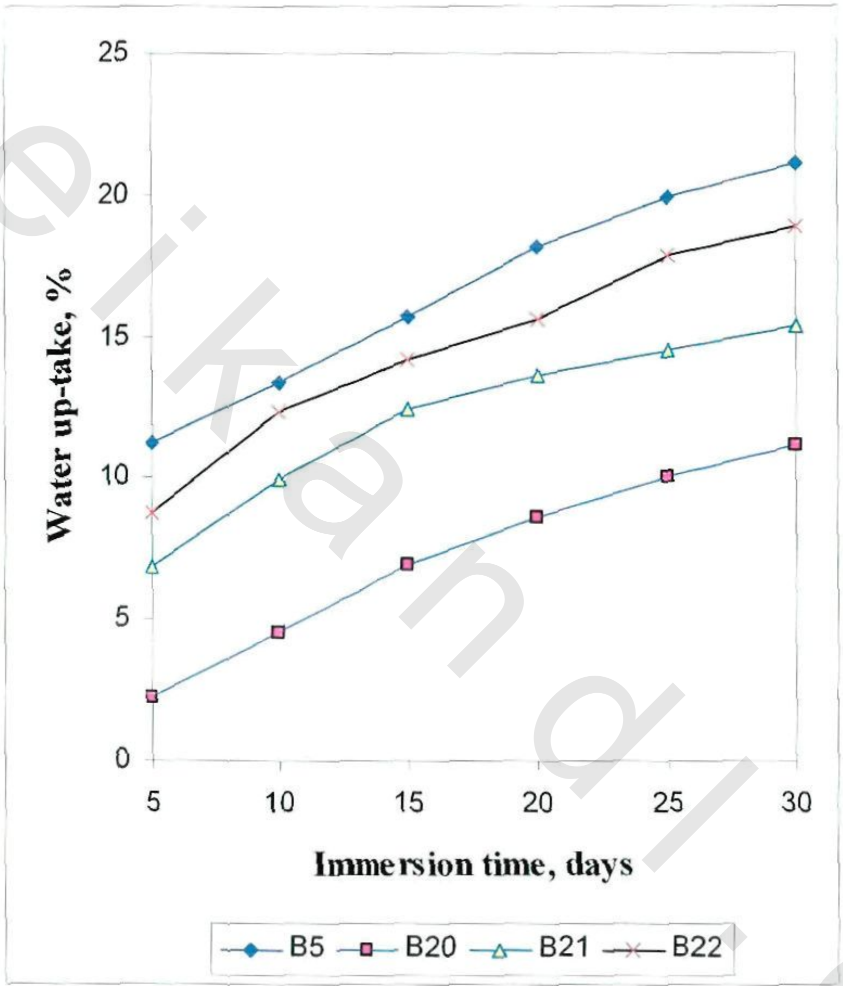


Fig. (4.26): The variation in water up-take (%) with time of immersion of group V

Corrosion resistance results of the immersed films in sea water for 28 days, are given in the Table (4.46), while the photos of the scribed coated steel panels at the end of test period are showed in Fig. (4.27).

Table (4.46): Corrosion resistance tests for paint films of group V

Test \ Formula No.	B5	B20	B21	B22
Corrosion resistance (1)	s.t.	b	s.t.	m.t.
Degree of blistering (2)	8F	10	6F	6M
Corrosion scratch test (3)	B	A	C	B

1. ***b:*** Bright surface; ***c:*** clean; ***v.s.t***: very slight tarnishing; ***s.t.:*** slight tarnishing; ***m.t.:*** medium tarnishing; ***h.t.***: high tarnishing and ***h.t.p.:*** high tarnishing and pitting.
2. It is graded on a scale from ***10*** to ***0***, where ***10*** no blistering and ***0*** for largest blisters and frequency denoted by ***F, M, MD*** and ***D*** (few, medium, medium dense and dense) respectively.
3. ***A-E***: Corrosion just in the scratch but differs in the adhesion of the film around the scratch; ***A = Gt0, B = Gt1, C = Gt2, D = Gt3, E = Gt4.***

The above results show a significant superior performance of formula (B20) where no sings of blisters in the paint film and no signs of corrosion have been observed under the paint film, while those containing zinc phosphate (B21) and zinc chromate (B22), exhibit corrosion resistance (slight tarnishing and medium tarnishing respectively) and the degree of blistering (6F and 6M respectively).

Weight loss measurements are giving in Table (4.47) and represented graphically in Fig. (4.28).

Table (4.47): Weight loss measurements (mg/cm^2), for steel panels under paint films of group V

Time (days) / Formula No.	10	20	30	40	50	60
B5	0.115	0.210	0.396	0.568	0.790	0.971
B20	0.016	0.039	0.072	0.118	0.164	0.241
B21	0.039	0.079	0.138	0.203	0.270	0.380
B22	0.042	0.119	0.184	0.230	0.307	0.425

Table (4.47) show that weight loss results goes parallel to those obtained with corrosion tests, where formula (B20) is the best with the value of weight loss (0.241 mg/cm^2) under the paint film, after 60 days of immersion of coated steel panels in artificial sea water, while it is (0.425 mg/cm^2) for sample B22, which contain zinc chromate as anti-corrosive pigment.

A comparative study of corrosion inhibition efficiency of coating formulation B20 containing 0.1% 3-MMT inhibitor and those containing zinc phosphate pigment B21 and zinc chromate pigment B22 are plotted in Fig. (4.29).

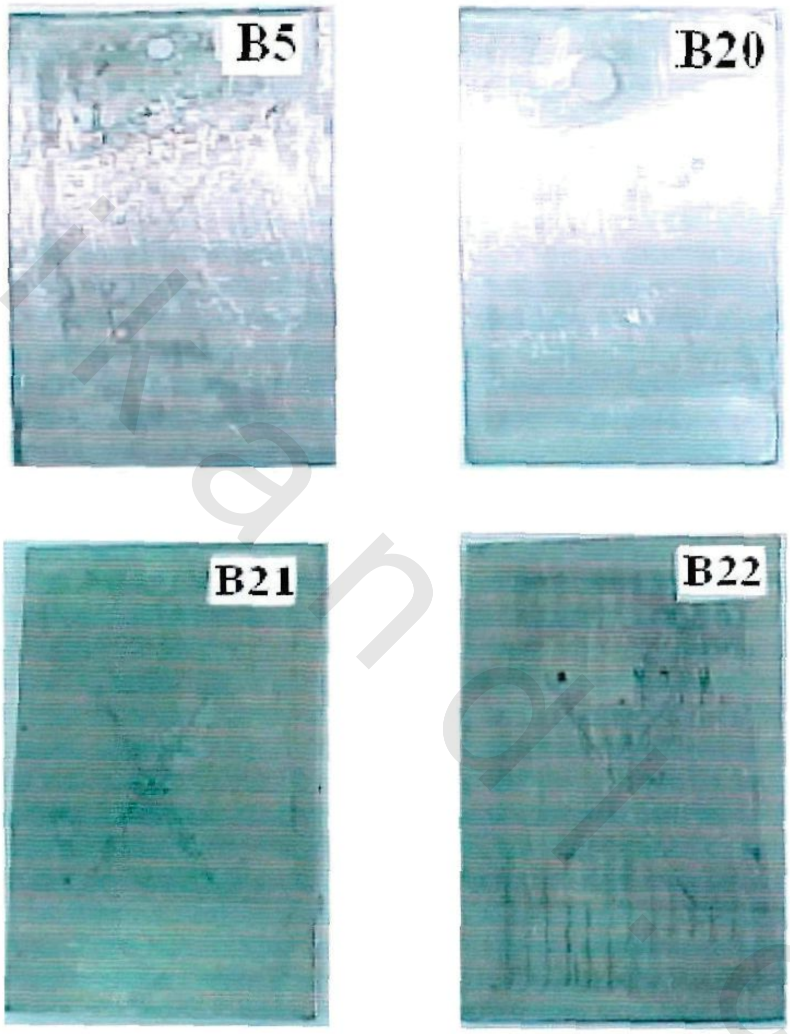


Fig. (4.27): Corrosion progress under paint films of group V after 28 days immersion in artificial sea water

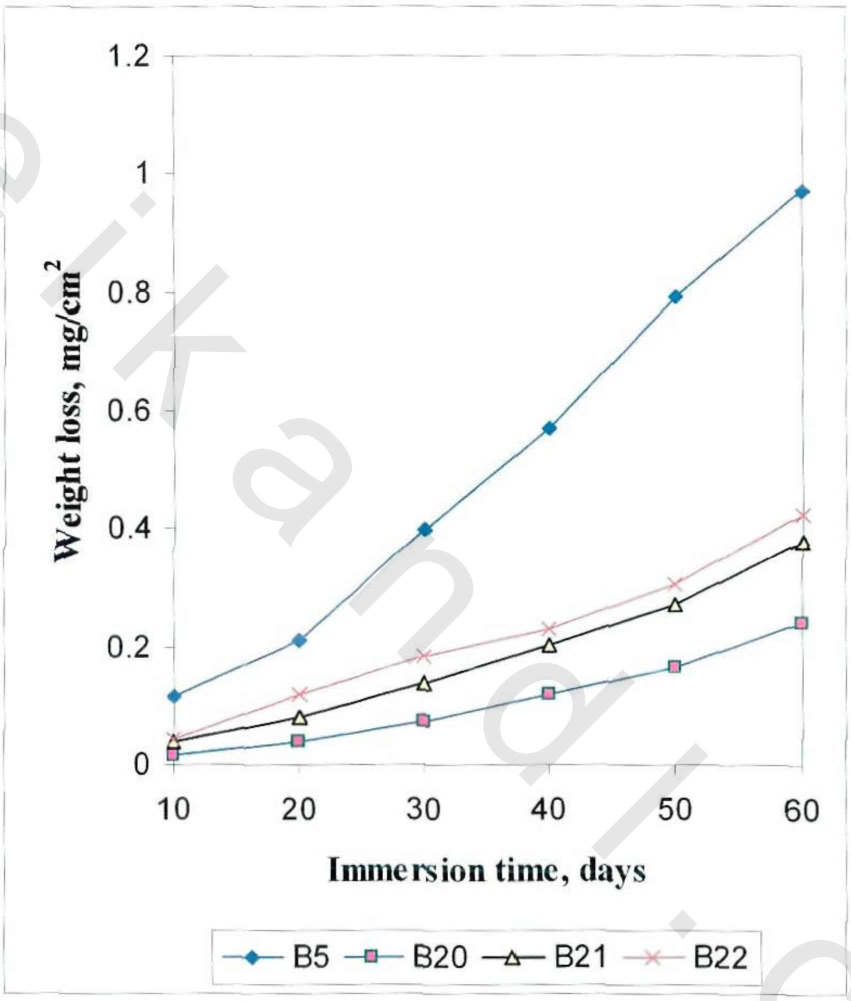


Fig. (4.28): The dependence of weight loss on the immersion time for paint formulations of group V

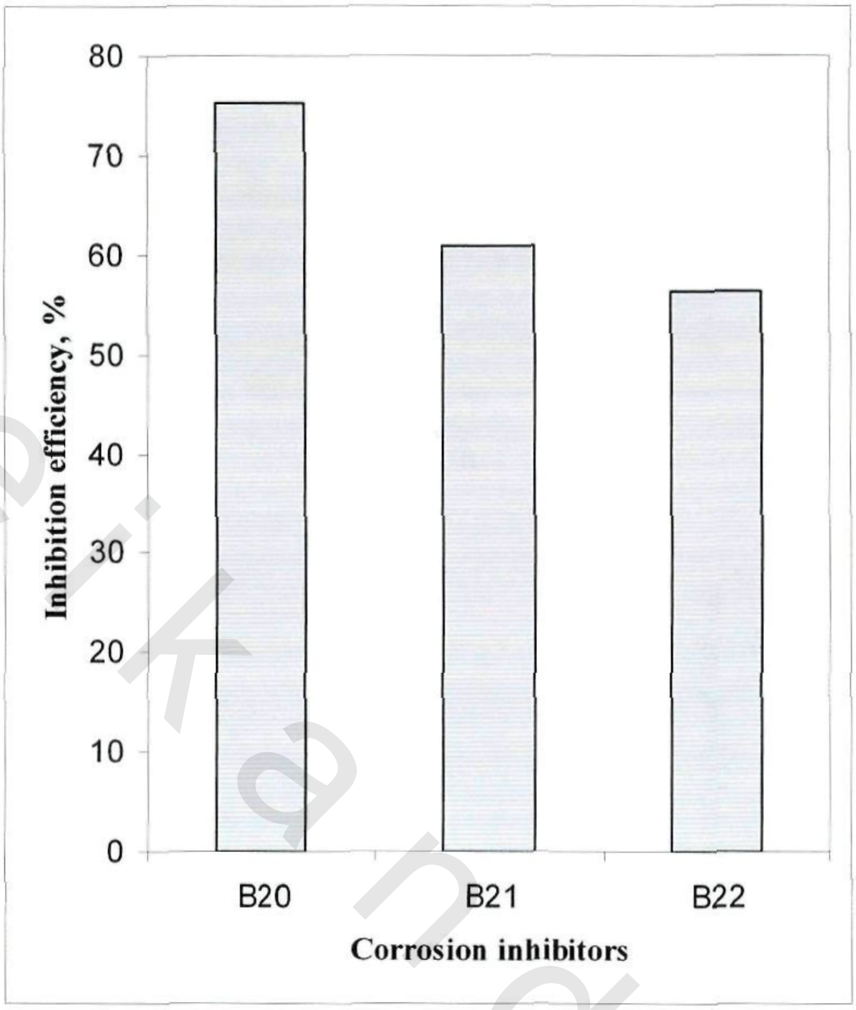


Fig. (4.29): Corrosion inhibition efficiency of paint samples of group V

Conclusions

- Highly efficient and friendly to environment water-borne anti-corrosive paints can be obtained using organic emulsified of 3-MMT adduct as corrosion inhibitor.
- Water-borne coatings formulated with zinc chromate and zinc phosphate generally showed inferior inhibition performance with respect to those formulated solely with emulsified of 3-MMT adduct.