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ECO-FRIENDLY WATER BASED PRIMER BASED ON NATURAL CORROSION INHIBITOR

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1. ABSTRACT

The aim of this study is to examine the performance of some natural products against corrosion. We tested Roselle, Ginger and Pomegranate peel (inherbs& extract forms) as corrosion inhibitors in paint industry. These inhibitors were added to primer formulation based on acrylic emulsion. The primer was pigmented with zinc phosphate. The study is extended to replace the zinc phosphate pigment with the natural products. The structures of the aqueous extract of natural products were analyzed by GC-MS spectra. Many international standard methods of corrosion testing were implemented; rusting, blistering, scribe failure after subjecting the steel panels to corrosive media (3.5 % sodium chloride solution). Also, mechanical and optical testing was conducted, e.g. hardness, cross-cut adhesion, cupping test and impact test were also evaluated.

The study concludes that natural corrosion inhibitors, in herbs or extract form can replace zinc phosphate pigment without deficiency of anticorrosion performance. This makes the primer more Eco-friendly and cost effective.

Keywords: ***Natural corrosion inhibitor, Primer, Herds.***

2-INTRODUCTION

Primers are common term for coating materials, which are applied before the topcoat and which have to fulfill different duties depending on the substrate properties. In the case of iron and steel, they have the outstanding function to insure corrosion protection. The anticorrosive primers economically rank among the most important coating materials, because they contribute decisively to maintain durable industrial and transport infrastructure. They are generally equipped with anticorrosive pigments like zinc phosphate, zinc dust, organic corrosion inhibitors, micaceous iron oxide … [1].

The use of water as solvent in air-drying corrosion-inhibiting primers (as well as finishes) has been a desirable aim but has proved to be very intractable problem. Much work has been done using conventional emulsion type systems but the very appreciable amount of water soluble has proved a stumbling block. Water-soluble types have been used for some years but these are cured by stoving [2.

For an inhibitor to be an effective protector against metal corrosion, it should be readily adsorbed on the metal surface through either physisorption or chemisorption processes. Either of these adsorption processes depends primarily on the physicochemical properties of the inhibitor group such as functional groups, electronic density at the donor atom, molecular structure, etc. For instance, organic molecules, which have had a wide applicability and that have been extensively studied and used as corrosion inhibitors, often contain nitrogen, oxygen, and sulfur atoms, as well as multiple bonds in their molecules [3, 4].

Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the used inhibitor must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly chemical. One of the sources of these cheap and clean inhibitors is plants.

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment.

Several reports are available on the various natural products used as green inhibitors. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors.

However, most of inhibitors have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (mill molar solutions). Many recent researches [5-12] have adopted this trend and carried out their work on naturally occurring substances. Promising results were obtained in previous work in this field.

The objective of this work is to study the effect Roselle, Ginger and Pomegranate peel (in herbs& extract forms) as corrosion inhibitors in paint industry.

3-EXPERIMENTAL

3.1. Preparation and extraction of the plant extract

3.1.1. Roselle Extraction:

Each plant materials [kenaf(Hibiscus cannabinus L.) seeds, roselle (Hibiscus sabdariffa L.] seeds and roselle calyxes) were grounded into fined powder using grinder to reduce the particles size respectively. The dried sample powders (500 g) were placed in a 2000 mL round-bottom flask with 1300 mL of deionised water, respectively in order to carry out hydro distillation for 4 hours or until there was no more essential oil yield. After 4 hours, the liquid retentate from each hydrodistillation were centrifuged at 4500 rpm for 20 minutes and the supernatant was filtered using filter paper to obtain a clear solution of water extract. The collected filtrates were then undergone rotary evaporation at 45°C using rotary evaporator until sticky extracts were obtained. The sticky extracts obtained were oven dried at 65°C for 1 day to remove excessive water. It was then kept at -20°C prior to further use. [13].

3.1.2. Ginger Extraction:

Ginger (Z. officinal Roscoe) rhizomes were purchased from the local market. One kilogram fresh ginger rhizome was cleaned, washed under running tap water, cut into small pieces, air dried and powdered. 125 g of this powder were macerated in 1000 ml of distilled water for 12 h at room temperature and were then filtered. The concentration of the extract is 24 mg/ml [14].

3.1.3. Pomegranate Peel Extraction:

Preparation of Raw Material: The samples were collected and washed thoroughly with water to remove any impurities. After drying at room temperature, the samples were ground into powder with the help of grinder.

Extraction of Crude Dyestuff: 100 g of sample was weighed and taken in a round bottom flask and 500ml of solvent (ethanol / water) in the ratio 40:60 was added to it. The flask was heated in a water bath at 60°C for 60mins.The solution was then filtered to obtain crude dyestuff.

Purification of Crude Dyestuff: The crude dyestuff is distilled to get 1/3rd of the solution using the Soxhlet apparatus at 70°C for 3hrs. In this process ethanol is recovered and the concentrated dye is obtained. The solution is kept overnight at room temperature for precipitation. The precipitation in ethanol / water is obtained by decanting the solution. The obtained particles are dried in the oven overnight at 60°C. Water was added in the

Soxhlet apparatus. By addition of water, the boiling points of the compounds are lowered, allowing them to evaporate at lower temperatures [15].

3.2. Materials and methods

3.2.1. (Table 1) The chemical composition of water based acrylic emulsion primer:

Ingredient	% (by weight)
Styrene acrylic	6
Titanium dioxide	3
Zinc phosphate	5
The rest (antifoam, wetting and dispersing, preservative…)	86
	100

(Table 2) The physical constants of the used emulsion paint as follows:

Binder type	Styrene acrylic
Solid content	69.275 %
Specific Gravity	1.7248
Solid by volume	48.6427
Drying time	30 min.

This emulsion paint was kindly provided from local Company of Egypt.

3.2.1. Preparation of the modified protective coatings.

The dried herbs were grinded by a mill and then passed through a series of sieves to obtain particles with size 32 µ. The grinded herbs were mixed with the coating base by concentration, namely 1 % w/v. The coatings of herb concentration was then applied to the steel coupons by brush and lifted to dry for further testing.

3.2.2. Preparation of steel panels (Procedure D solvent cleaning).

Using clean, lint- less cloth with mineral spirits vigorously rub the panel surface (7.5 X 13.5 cm) until all soluble and loosely adhering soil has been removed, flush with clean solvent. Dry at room temperature for 24 hrs.before use or storage. [16].

3.2.3. Evaluating the degree of rusting on painted steel surfaces [17].

3.2.4. Evaluating the degree of blistering of paints [18].

3.2.5. Evaluation of painted or coated specimen subjected to corrosive environments [19].

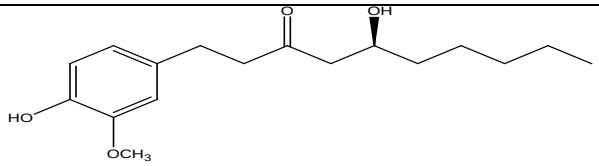
3.2.6. Mechanical and optical testing techniques.

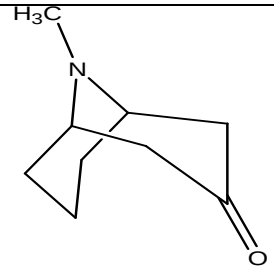
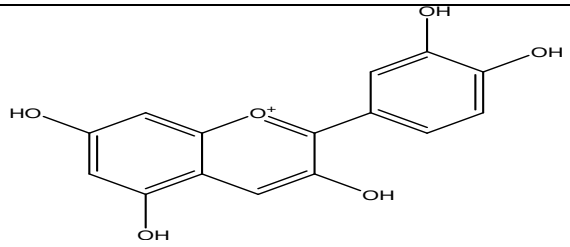
In order to elucidate the properties of the modified coatings, the coated samples were exposed to some important testing techniques and measurements such as Cross Hatch testusing Multi-Cross Cutter 295/V, with 11 edges, cutting distance 1 mm (ERICHSEN GmbH & Co., Germany), thickness of the dry coated films using digital coating thickness gauge Elcometer 456 (Elcometer Instruments GmbH, Germany), gloss measuring by utilization of gloss measuring device PICOGLOSS 560 MC-XS (ERICHSEN GmbH & Co., Germany), testing of hardness by indentation hardness tester model 263(ERICHSEN GmbH & Co., Germany) and impact testing using impact tester model 304(ERICHSEN GmbH & Co., Germany). The color data were investigated using Flash 100 spectrophotometer [20].

3.2.7. Selection and assessment of natural product extracts used by Gas Chromatography / Mass Spectrometry (GC/MS)

The analyses were performed on an Agilent 7890A GC/5975C MSD system at Central Laboratory for Environmental Quality Monitoring (CLEQM) - National Water Research Center (NWRC). Mass-Hunter WorkStation software was used for structure verification.

Table (3): Assessed natural product extracts

No.	Name	Molecular Formula	Molecular Weight	Molecular Structure
1	Ginger	$C_{17}H_{26}O_4$	294.18	

2	**Pomegranate Peel**	**$C_9H_{15}NO$**	**153.12**	
3	**Roselle**	**$C_{15}H_{11}O_6^+$**	**287.24**	

3.2.8. Preparation of paint formulations.

Fourteen emulsion paint formulations are prepared according to table (4)

Table (4) Emulsion paint formulations

Formulation No.	Description	Formulation No.	Description
With $Zn_3(PO_4)_2$		Without $Zn_3(PO_4)_2$	
1B	Blank (water based acrylic emulsion primer)	8B	Blank (water based acrylic emulsion primer)
2NGin	Formulation I + 1.0 % Gin. powder	9NGin	Formulation I + 1.0 % Gin. powder
3NRos	Formulation I + 1.0 % Ros. powder	10NRos	Formulation I + 1.0 % Ros. powder
4NPom	Formulation I + 1.0 % Pom. powder	11NPom	Formulation I + 1.0 % Pom. powder
5 EGin	Formulation I + 1.0 % Ginger extract powder	12 E Gin	Formulation I + 1.0 % Ginger extract powder
6 ERos	Formulation I + 1.0 % Ros. extract powder	13 E Ros	Formulation I + 1.0 % Ros. extract powder
7 EPom	Formulation I + 1.0 % Pom. extract powder	14 EPom	Formulation I + 1.0 % Pom. extract powder

i. B Blank

ii. N natural herbs powder

iii. E extract products powder

iv. Ginger (Gin.)

v. Pomegranate Peel (Pom,)

vi. Roselle (Ros.)

4-RESULTS AND DISCUSSION

The aqueous extract of Ginger, Roselle and Pomegranate peel has been studied as possible source of green inhibitor for the corrosion of mild steel in 1M HCl [21, 22].

These previous study gave good results for the value of the corrosion inhibition efficiency which reaching to 91%, 89% and 85% for 1(w/v) % extract powder of Ginger, Roselle and Pomegranate peel respectively [21, 22].

On the other hand, we have been using in this study all natural products extracted compounds in the form of powder where the previous study also proved that we should use anti-bacterial materials (biocide) in order to be saved aqueous extract compounds for more than one years.

In this study also tried to use natural herbs powder after grinding process and try to reach smaller size as far as possible.

As a result of this we try to study the effect of this natural product extract and herbs powder as emulsion for corrosion inhibition in paint industry.

4.1. Evaluating natural product extracts by Gas Chromatography / Mass Spectrometry (GC/MS).

GC/MS give light on the structure of natural product extracts which is obtained from the extraction of (A) ginger, (B) Pomegranate Peel and (C) Roselle extract. The GC/MS spectrum exhibits the retention time for “Granatonine" (**$C_9H_{15}NO$ - 153.12)** 6.33 and 11.78, for ("Gingrol") (**$C_{17}H_{26}O_4$ - 294.18)** 25.87 where for (R "Anthocyanins Derivatives") (**$C_{15}H_{11}O_6^+$ - 287.24 / 738.31**) 65.18 minutes (Fig.1).

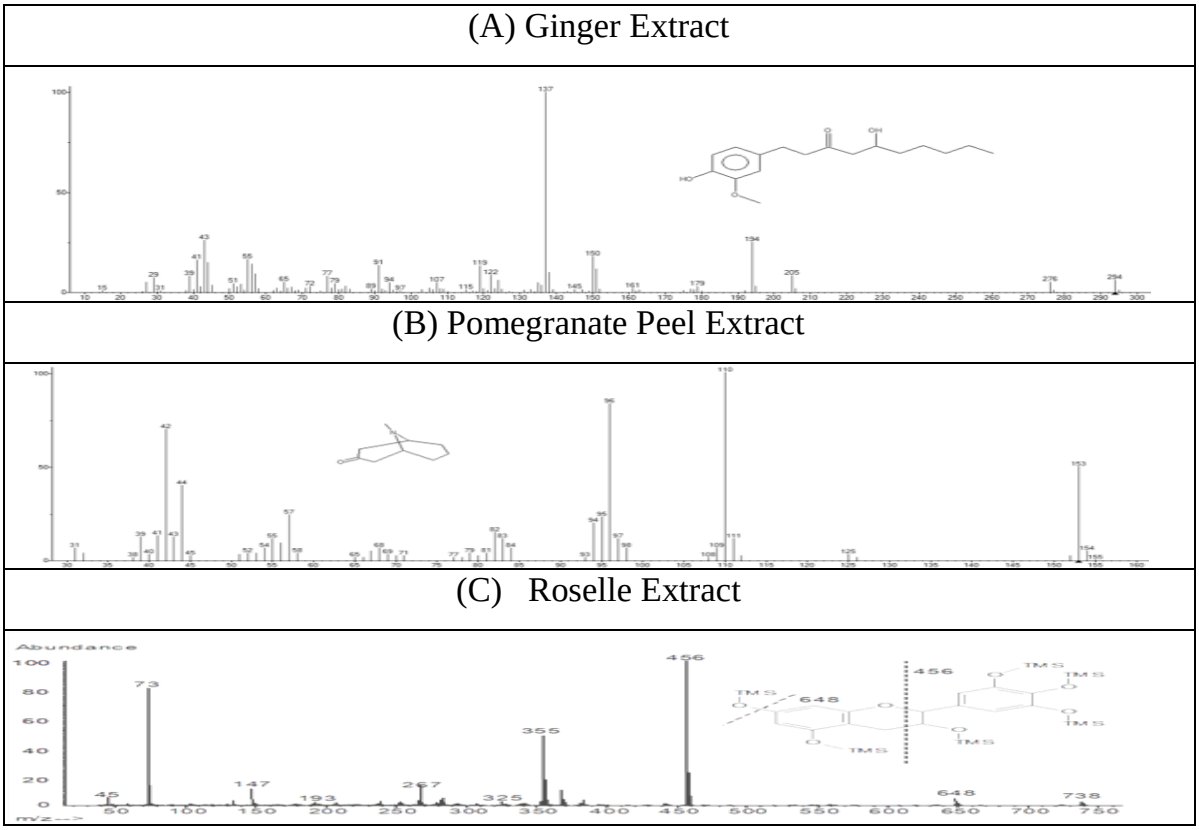


Figure (1): GC/MS Scan of (A) Ginger extract, (B) Pomegranate Peel Extract and (C) Roselle Extract.

4.2. Anticorrosive emulsion paint with Ginger, Roselle and Pomegranate Peel as natural corrosion inhibitor.

4.2.1. Evaluation of aqueous extract of Ginger, Roselle and Pomegranate Peel with Water based acrylic emulsion primer.

It is well known that emulsion paints are frequently used for architectural applications. It was thought to improve the corrosion resistance of the emulsion paint by adding a 1% dose of natural corrosion inhibitor with and without zinc phosphate as inhibitive pigment. We used previously ginger, roselle and pomegranate peel extract for improving the corrosion resistance of solvent based epoxy primer. In this study, we used 0-5 % zinc phosphate in the formulation of the emulsion paint and added 1 % ginger, roselle and pomegranate peelextract as natural corrosion inhibitor in powder forms.

Eight emulsion paint formulations are prepared according to table (4) where formulations 1B, 5Egin. 6 E Ros. & 7EPom with $Zn_3 (PO_4)_2$ and 8B, 12Egin. 13 E Ros. &14EPom without $Zn_3 (PO_4)_2$.(Fig.2andTable5)

The above formulations were applied to steel panels as described before and submerged in the glass box container for 28 days. The following (Table5) illustrates the testing of blistering, rusting and scribe failure according to ASTM standards. All the samples are rated 10 in scribe rating, which means that the creep age from scribe is zero, i.e. the corrosion resistance is satisfactory.

The blistering evaluation indicates that all samples are better than the blank formulation (1B and 8B). The rusting indicates that formulation 5Egin. 6 E Ros. & 7EPom are the best and followed by formulation 12Egin. 13 E Ros. &14EPom.All these formulations are much better than formulation (1B and 8B) "the blank sample". Previous results are consistent with the results of measurements of the mechanical properties (Fig3. and Tables 6, 7).

Table (5) Scribe rating, blistering and rusting evaluation

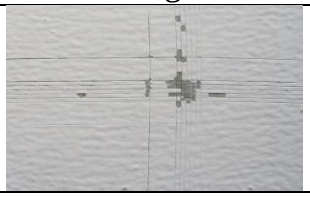
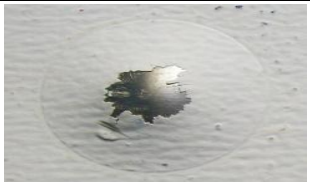
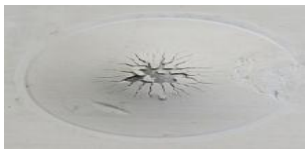
Formulation No.	Scribe rating	Blistering, size & frequency	Rusting rat	Formulation No.	Scribe rating	Blistering, size & frequency	Rusting rate
With $(Zn)_3 (PO_4)_2$				Without $(Zn)_3 (PO_4)_2$			
1B	10	6M	4P	8B	10	6MD	1P
2NGin	10	8F	9S	9NGin	10	8M	8P
3NRos	10	8F	8S	10NRos	10	8M	7P
4NPom	10	8MD	9S	11NPom	10	8D	8P
5EGin	10	6F	9S	12EGin	10	8D	8S
6ERos.	10	6F	9S	13ERos.	10	6D	8P
7EPom	10	6F	9S	14EPom	10	6D	8P

Fig.(2) Water based primer + (Gin. Ros. And Pom Extract Powder)

without $(Zn)_3 (PO_4)_2$		With $(Zn)_3 (PO_4)_2$	
Original Sample	28 Days	Original Sample	28 Days
Blank (water based acrylic emulsion primer)			
			
8B	8B	1B	1B

Formulation I + 1.0 % Gin. Extract Powder			
			
12EGin	12EGin	5EGin	*5EGin*
Formulation I + 1.0 % Ros.Extract Powder			
			
13ERos	13ERos	6ERos	6ERos
Formulation I + 1.0 % Pom. Extract Powder			
			
14 EPom	14 EPom	7EPom	7EPom

Fig.3. Cross Hatch,Cupping and Impact test evaluation of (Ginger, Roselle and pomegranate peel extracts) in extract form.

Formulation No.	cross cut test/adhesion 1mm cutting distance	cupping test cracking of coating	ball impact test cracking of coating
1B			
5EGin			

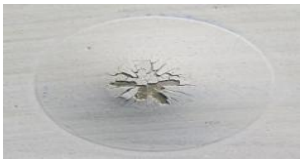
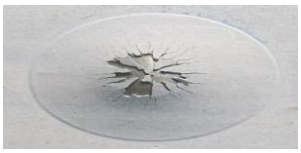
6ERos			
7EPom.			

Table.6.The measurements and testing results of (Ginger, Roselle and pomegranate peel extracts) in extract form.

Sample	**Gloss meter-60°**	**film thickness recommended**	**impression hardness**	**cross cut test/adhesion** 1 mm cutting distance	**cupping test** cracking of coating	**ball impact test** cracking of coating
1B	1	98 µm	45.45	5	**≥ 5 mm**	High cracks
5Egin.	3	147 µm	76.92	1	**≥ 5 mm**	low cracks
6Eros.	3	149 µm	66.6	2	**≥ 5 mm**	low cracks
7EPom.	4	200 µm	50	2	**≥ 5 mm**	medium cracks

Table.7.shows the optical properties of the Datacolor obtained from spectrophotometer of the (Ginger, Roselle and pomegranate peel extracts in extract form.

Sample	**Color tools**			
	DL	**Da**	**Db**	**DE**
1B	0	0	0	0
5EGin	-9.4	2.19	8.62	12.94
6ERos	-9.27	-0.66	3.07	9.79
7EPom.	-20.29	-0.7	1.06	20.33

4.2.2. Evaluation of herbs of Ginger, Roselle and Pomegranate Peel with Water based acrylic emulsion primer.

Eight emulsion paint formulations are prepared according to table (4) where formulations 1B,2Ngin. 3NRos. &4N Pom with $Zn_3 (PO_4)_2$ and 8B, 9Ngin. 10N Ross. & 11N Pom. without $Zn_3 (PO_4)_2$.Photographs of the tested article after about 672 hours are showing in (Fig.4).

Also results all the samples are rated 10 in scribe rating, which means that the creepage from scribe is zero, i.e. the corrosion resistance is satisfactory.

The blistering evaluation (Table 5) indicates that all samples are better than the blank formulation (1B and 8B). The rusting indicates that formulation 2Ngin. 3NRos. &4N Pomare the best and followed by formulation 8B, 9Ngin. 10N Ros. & 11N Pom. It should note that the results indicate an excellent performance of all these formulations when compare with blank samples (1B and 8B).

Previous results are consistent with the results of measurements of the mechanical properties (Fig.5 and Tables 8-9).

On the other hand, the results of aqueous extract are not far from the results of herbs, which favored the use of herbs where the economic cost will be much less and I think the results will be more better when we can reach the size of Nano.

Fig. (4) Water based primer + (Gin. Ros. andPom herbs)

Without $(Zn)_3 (PO_4)_2$		With $(Zn)_3 (PO_4)_2$	
Original Sample	28 Days	Original Sample	28 Days
Blank (water based acrylic emulsion primer			
			
8B	8B	1B	1B
Formulation I + 1.0 % Gin. powder			
			
9NGin	9NGin	2NGin	2NGin
Formulation I + 1.0 % Ros. powder			

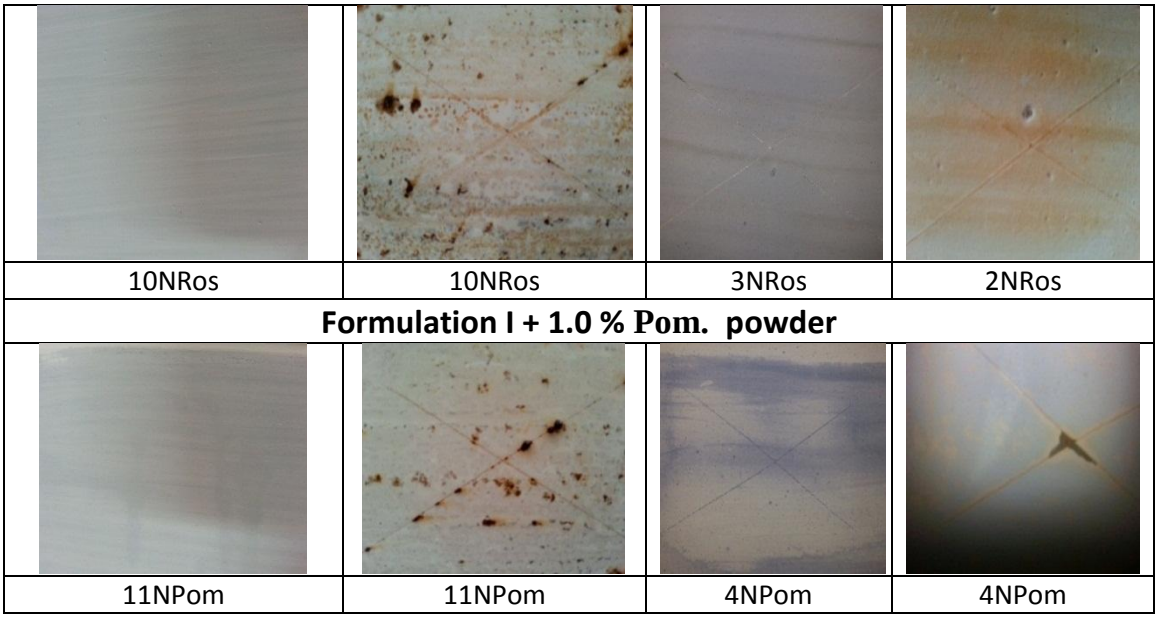


Fig.5. Cross Hatch,Cupping and Impact test evaluation of (Ginger, Roselle and pomegranate peel) in herbs powder.

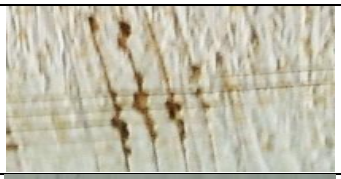
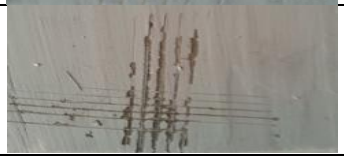
Formulation No.	**cross cut test/adhesion** 1mm cutting distance	**cupping test cracking of coating**	**ball impact test cracking of coating**
1B			
2NGin			
3NRos.			
4NPom.			

Table.8.The measurements and testing of mechanical results of (Ginger, Roselle and pomegranate peel) in in herbs powder.

Sample	**Gloss meter- 60°**	**film thickness recommended**	**impression hardness**	**cross cut test/adhesion** 1 mm cutting distance	**cupping test** cracking of coating	**ball impact test** cracking of coating
1B	0	132 µm	31.25	4	**≥ 5 mm**	High cracks
2NGin.	0	145 µm	40	4	**≥ 5 mm**	No appearance of cracks
3Nros.	2	65 µm	50	1	**≤ 5 mm**	No appearance of cracks
4NPom.	3	70 µm	50	4	**≥ 5 mm**	medium cracks

Table.9.shows optical properties of the Datacolor obtained from spectrophotometer of the (Ginger, Roselle and pomegranate peel) in in herbs powder.

Sample	**Color tools**			
	DL	**Da**	**Db.**	**DE**
1B	0	0	0	0
2NGin.	-1.02	0.01	1.66	1.95
3Nros.	-13.72	-2.61	-1.88	14.09
4NPom.	-19.23	-0.13	-1.86	19.32

5-CONCLUSIONS

1- Roselle, ginger and pomegranate peel (in herbs & extract forms) have shown their capability to protect steel from corrosion.

2- The results of blistering, rusting and scribe failure show that natural product extract and herbs powder as emulsion for corrosion inhibition are much an excellent performance than the blank sample.

3- By using natural product extract gives better results than herbs powder in the present of Zincphosphate.

4- Moreover, the results of aqueous extract are not far from the results of herbs, which favored the use of herbs where the economic cost will be much less and I think the results will be more better when we can reach the size of Nano.

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