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Comparative study of rust prevention performance of different rust preventive oils based on type of carriers

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Abstract : *Rust preventive oils (RPO) plays vital role in rust protection of finished and in process products storage. Type of carriers used in the RPOs will have great impact on rust prevention period. The temporary rust protection oils isolate the metallic surfaces from the aggressive media such as moisture, salts and acids. In the present study, different types of RPOs and their behavior on rust protection of rolling bearings and its components is analyzed. Commercially available RPOs are compared based on type of carrier and its impact on rust protection duration in simulated lab conditions. Detailed study was conducted to understand type of carrier and its impact / relationship with protection period based on various accelerated lab conditions like humidity chamber, salt spray test. Initial samples were measured for key performance parameters like viscosity and identification given for further study. The comparison is made based on pre-decided relative ranking.*
Keywords - *rust preventive oil; rusting, rust protection; RPO carriers*

I. Introduction

Permanent rust protection can be achieved in many ways using special materials, special treatments like galvanising, special coating etc. However, many times rust protection is required only for storage purpose until the product is put into application. Other considerations like permanent rust protection cannot be applied between the various stages of manufacturing or on components which are used in application where permanent protections may have negative effects.

Present study is focused on temporary rust protection which is used to prevent finished or semi-finished metal components especially rolling bearing. Bearing components are very sensitive to rust in the application and any stains marks or rust forms on the surface it is not advisable to use in the application. Rust formation in the bearing or bearing components is having detrimental effect on bearing performance. The temporary protection isolates the metallic surfaces from the aggressive media such as moisture, salts and acids [1].There are three main requirements of an effective temporary rust preventive protections. Firstly, the substance must bind itself to the metal surface and inhibit oxidation. Secondly, the film should give mechanical protection against moisture. And finally, the method of application must ensure the entire surface of the metal is evenly covered by the rust preventive agent. In temporary rust protection, components are usually protected by oil which contains organic compounds especially fatty acids. These compounds form a physical barrier between the metal substrate and the corrosive environment [2]these fatty acid molecules have a long water-repelling hydrocarbon "tail" and a "head" that has a strong affinity for the metal surface [3,4]. The long, thin molecules line up roughly parallel to each other and perpendicularly to the metal surface, forming a layer that is essentially impervious to water and oxygen. However, given time, moisture will still diffuse through both the oil layer and the rust inhibitor layer — but it will take longer because of the water repelling nature. Mayne proposed that the electrical conductivity of layer is the variable that controls the degree of corrosion protection [5].

RPO consists of rust inhibitor and carrier. Rust inhibitor provides the chemical, and possibly mechanical protection of the metal and carrier ensures the efficient spread over the complete metal surface. The comparison of protection efficiency of individual constituents (Rust inhibitor) with the oil under identical experimental conditions shows that the individual constituents are less efficient than the carrier of the inhibitors. This observation indicated that these constituents are not solely responsible for rust inhibition [6].

We have created simulated accelerated corrosive environment like salt spray and humidity chamber tests for on available commercial RPO's testing to make a relative rankings based on their test results.

Four Ball-Test is conducted for understand lubricity effect in applications like rolling bearings as it is expected that RPO must provide lubricity to reduce initial wear.

II. Comparative Ranking Methodology

The study was done based on relative ranking methodology. This method is adopted due to complexity in correlating the actual environment performance condition with accelerated environment tests. The accelerated corrosive environment tests were conducted at standard test environment to derive the ranking and to conclude the study. We have selected samples in this study are being used for different application with common testing conditions. We have assigned weightage to performance parameters test based on severity of test conditions and relative importance in rust protection. Ranking was given based on actual test results. Sample gives longer rust free protection is considered as relatively better performing assigned highest rank and shorter duration protection against rusting is assigned lower ranking.

Table – 1: Performance tests weightage

Sr. No.	Type of test	Weightage	Remark
1	Humidity chamber test	40	Accelerated rust test (Most severe test as selected test samples / products are not coming directly in contact with wet and salty environment).
2	Salt spray test	30	Accelerated rust test
3	Viscosity	20	Determination of adhesive properties
4	Four ball test	10	Lubricity requirement for a particular requirement
	Total	100	

Table – 2: Ranking Guidelines

Description.	Ranking	Remarks
Low	1	Lowest rust protection duration / Performance
Moderate	2	Intermediate rust protection duration / Performance
Good	3	Highest rust protection duration / Performance

Table – 3: Scoring of samples test results

Weightage	Rank	Score
A	**B**	**A X B**

Interpretations of Score
Higher the score indicates better performing sample.
Lower score indicates, lower performing samples

III. Samples, test and test Procedures

3.1 Material and sample preparation

Four types of RPOs are considered for comparison which consists of different carriers like mineral oil, solvent, mix of solvent & oil and with VCI (Vapour corrosion inhibitor) additives.

Table – 4: Different type of RPO with its properties

Identification	Carrier type	Inhibitor	Flash point °C
A	Mineral oil	Salphonate based	166
B	Solvent	Salphonate based	80
C	Mixture of mineral oil & solvent	Salphonate based	> 60
D	Mineral Oil	Amines and VCI	> 150

Application method: Dipping method.
The test specimen material was carbon steel, and chemical composition (mass percent, %) as per the given Table 5.

Table 5: Chemical composition of the carbon steel %

Test material	**Composition**							
	C	S	Al	Cu	Mn	P	Si	Cr
Carbon steel	0.16	0.2	-	-	0.65	0.018	0.2	-

The size of each specimen was about 120 mm x 60 mm x 2 mm. The samples were polished with 2000 grit diamond, ultrasonically cleaned in methanol, dipped in the test oil for a minute, allowed to drain for two hours before put into test

3.2 FTIR sampling

An infrared spectrum helps to differentiate various chemical bonds of samples with absorption peaks which correspond to the atoms making up the samples. Each different material is a unique combination of atoms. Therefore, infrared spectroscopy can result in a positive identification of different kind of material.

An infrared spectrum (FTIR) is used in this study to determine type of base oil used in the RPO i.e relative proportions of Paraffinic, Naphthenic and Aromatic components present are determined as per Indian Standard 13155:1991 [7].FTIR is also used to verify potential corrosion inhibitors in the RPOs.
The FTIR spectrums of sample scans were collected for each sample at a resolution of 4cm-1over the wave number region 4000-550 cm-1, using a Spectrum Perkin Elmer.

3.3 Humidity cabinet

This test is an accelerated rust test under a controlled corrosive environment. It has been used, to produce relative corrosion resistance information for the test samples. The test was conducted as per ASTM D1748 for a specified number of hours as per the conditions i.e. 90 to 95% relative humidity with pH 5.5 to 7.5 at chamber temperature of 48 ± 1 °C in the test chamber (Make: Labin scientific instruments) with test condition.

Acceptance Criteria: Specimen considered fail, if rust area is less than Φ 1 mm^2 and first appearance of rust in the area which is 3 mm from all the edges of the specimen.

Fig1: Humidity chamber test set up

3.4 Salt spray

Salt Spray test is accelerated corrosion test; test was conducted as per ASTM B117. The specimens were positioned in such a way that 20 deg angle in vertical position which was parallel to the principal direction of horizontal flow of fog through the chamber by the support of glass tray. The test was conducted in a controlled environment with humidity of 90 to 98% with temperature maintained in 48°C ± 2°C for a maximum of 120 hrs per cycle. Total three tests had been conducted with four plates per samples were used. The concentration of salt solution is of 5% NaCl AND 95% distilled water.

Acceptance Criteria: Specimen considered fail, if rust area is less than Φ 1 mm^2 and first appearance of rust in the area which is 3 mm from all the edges of the specimen.

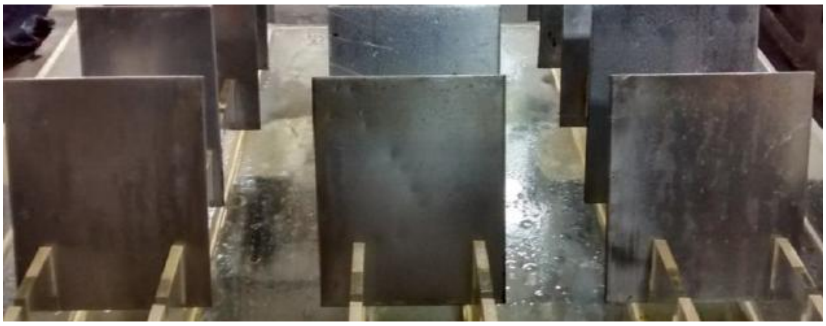

Fig 2: Salt spray test sample initial set-up

3.5 Viscosity

Viscosity is one of the critical physical properties for Oils used in industries and in RPO also, viscosity play a mojor role by RPO with a relatively low viscosity oil can be applied easily and removable. Inviceversa high viscous oil is difficult to apply and remove.

Parker Kittiwake heated viscometer is used to measure the oil viscosity at 40°C and programmed to calculate at 100°C temperature as per ASTM D445. Viscometer is a falling ball viscometer type. A 45 degree inclined tube is filled with the oil to be tested and then a steel ball is dropped into it. The measurement is then made by timing the period required for the ball to fall and is measured by equipment at 40°C. .

3.6 Lubricity

Four Ball - Test was conducted to determine the lubricity characteristics of RPO. Test conducted as per ASTM D4172 by applying 392 N load and sliding speed of 1200 rpm for 60 seconds using Φ 12.7 mm steel ball. The steel ball was rotated under load against three stationary steel balls immersed in the RPO. The lubricity of RPO was evaluated by the average wear depth of the three stationary balls in four ball test tribo-meter (Make: CETR).

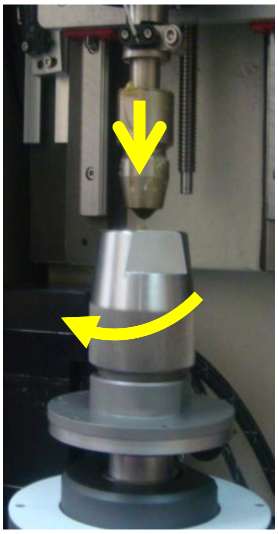

Fig 3: Four ball test arrangement

Acceptance Criteria: This is comparative analysis; comparison of average wears depth after test and ranking samples based on results.

IV. Result & Discussion

1.1 FTIR :

A typical formulation for rust preventive oil concentrate consists of a carrier as such mineral oil, whose structure is very complex. Mineral oils are differing from each other depending on the source of crude oil and refining process. Oils are distinguished based on the relative proportions of paraffinic, naphthenic and aromatic components present. The presence of one type or the other of these determines some of the physical properties of the lubricants, i.e. pour point, viscosity index, pressure-viscosity characteristics [8].

The calculation is performed manually by measuring the intensity of the peak at 1600 cm-1 for CA and 720 cm-1 for CP. Tangents are drawn in the spectra on either side of the peak being measured, and a vertical line is drawn through the peak minimum. The intersection of these lines gives the value of low intensity (I_0) and the intersection of vertical line with the peak minimum gives value of high intensity (I).

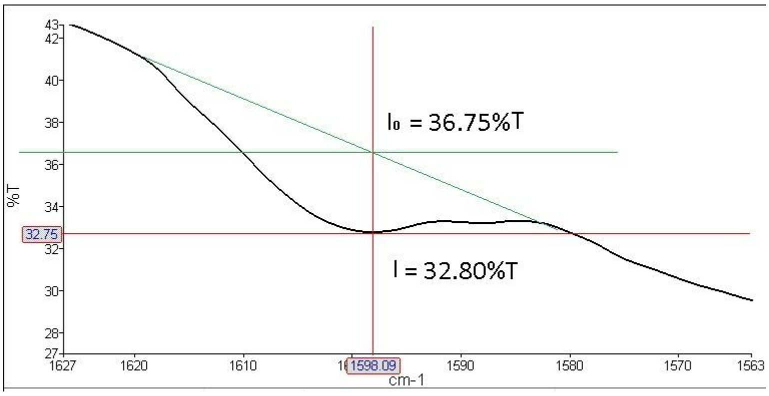

Fig 4: I_0 & I measurement

Formulae:

For CA	For CP	For CN
CA = 1.2 + 9.8 E	CP = 29.9 + 6.6 E	CN = 100 - (CA + CP)
E = [Log Io/ I] / d	E = [Log Io/ I] / d	
Where: d = path length (0.1)		

Table – 6: Determination of Aromatic (CA), Paraffinic (CP), and Naphthenic (CN) carbon

SAMPLE	AROMATIC SUBSTANCES %	PARAFFINIC SUBSTANCES %	NAPHTHENIC SUBSTANCES %
A	10	48	42
B	5	46	49
C	4	38	58
D	22	22	56

From the above table, proportions are measured and Napthenic is predominant in all the RPOs except sample A. Generally naphthenic oil has more polar characteristics than paraffinic oil, which makes naphthenic oil a better choice for use as a carrier in a rust preventive agent. From the table -6, Aromatic (CA), Paraffinic (CP), and Naphthenic (CN) carbon in mineral base oils are determined and sample B, C & D have dominant napthenic carbon structure, though sample –A has paraffinic structure. Generally paraffinic oils contain unbranched n-paraffin molecules that tend to form a wax at low temperatures and which increase the viscosity of the sample -A. Rust preventive agents that contain naphthenic oils are considerably more stable than emulsions formed with paraffinic oils [9] and to dissolve the large amount of additives, a naphthenic oil is preferred because it has better solubility properties than a paraffinic oil.

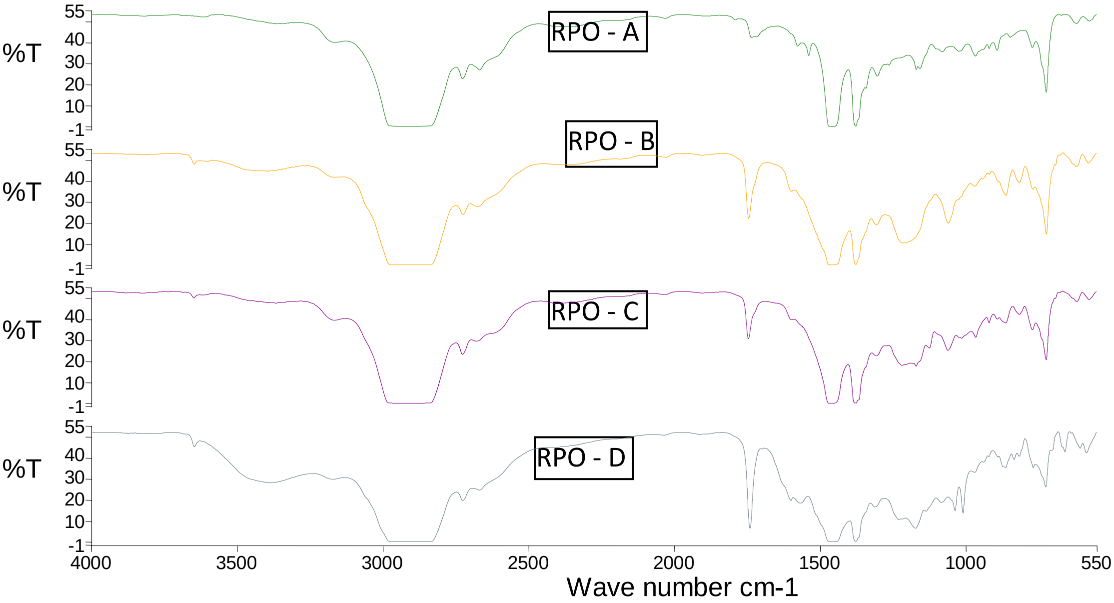

Fig. 5 IR spectrum of four type RPO's

The given four samples IR spectra are interpolated and by using software, we have identified possible structural unit and showing Sulphonate and amine group as a rust inhibition additive and MSDS of the samples are also suggest the same..

Table 7: Potential functional group of inhibitors present in the RPO's are mentioned below

NAME	POSSIBLE STRUCTURE	PEAKS
RPO – A	Sulphonate	1462 CM-1, 1378 CM-1, 1160 CM-1, 1046 CM-1, 892 CM-1
RPO – B	Sulphonate	1462 CM-1, 1378 CM-1, 1160 CM-1, 1046 CM-1, 892 CM-1
RPO - C	Sulphonate	1462 CM-1, 1378 CM-1, 1160 CM-1, 1046 CM-1, 892 CM-1
RPO - D	Amines	3450 CM-1, 1575 CM-1, 1185 CM-1, 715 CM-1

1.2 Humidity Chamber

Two cycles of test were conducted for all the samples Results are shown in below figure

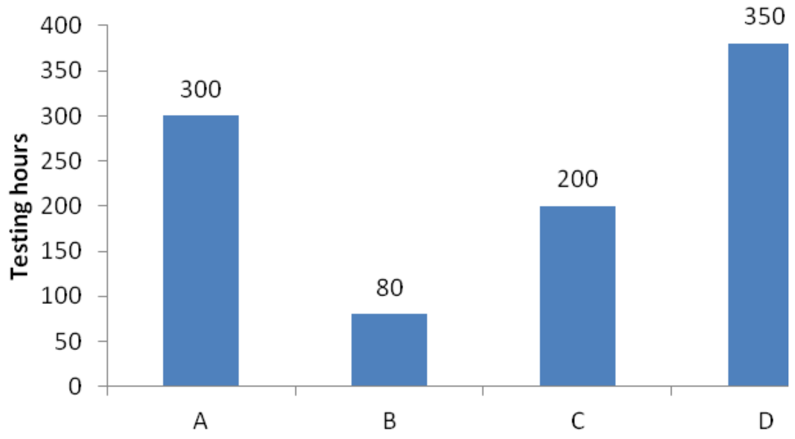

Fig6. Humidity chamber test

Based on test results, four RPO's applied specimen provided different corrosion protection in a similar test environment conditions. Sample - A & D had suppressed the rusting protection over a period of more than 300 hours especially sample – D had passed 350 hours. We assigned ranking of high to sample D & sample A as moderate. Sample – type D clearly shown indication of good rust control properties of the mineral oil based rust preventive oils. In the case of sample – C, there were rust marks on the surface, after 200 hours. On sample – B, rust / corrosion marks were visible after 80 hours. Sample C & Sample B assigned ranked of moderate & Low respectively.

1.3 ***Salt spray test:***

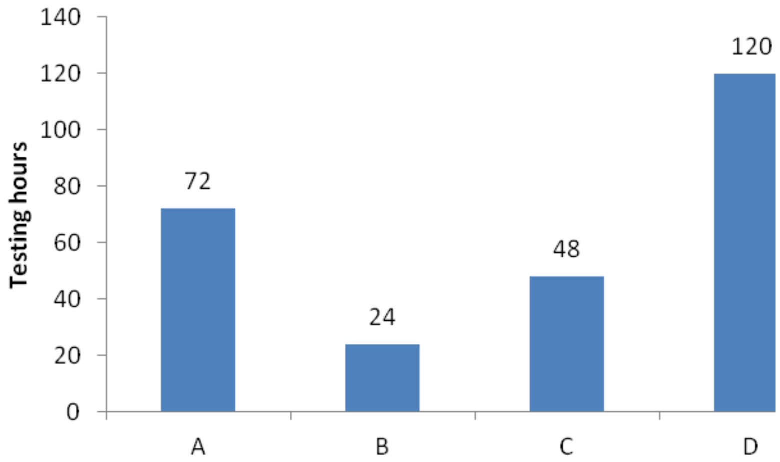

Fig7. Salt spray test result

Fig 8: Observations after 24 Hours

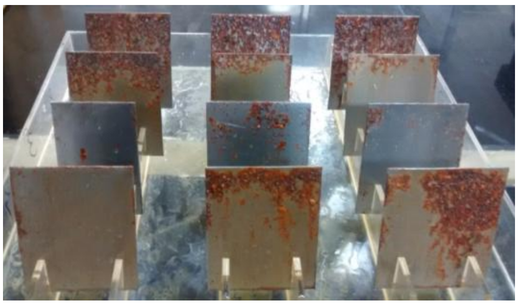

Fig 9: Observations after 120 Hours

Almost similar results observed for salt spray test and humidity chamber test. Sample – B is fully solvent based RPO, which evaporates and forms very thin protective film on the metal surfaces. Water droplets formation on the metal surface with thin film, breaks the film over the time. This may be the reason that sample

– B has very less life than others. We assigned ranking of high to sample D & sample A as moderate and Sample C & Sample B assigned ranked of moderate & Low respectively.

1.4 Viscosity:

Table 8: Viscosity of given samples

Sample Identification Number	Viscosity in cSt	
	At 40°C	At 100°C
A	160	15.0
B	2.5	-
C	11	3.0
D	22	4.0

Sample – A is higher viscosity oil compare to sample – B & C. Sample C, D & A results of salt spray and humidity chamber test are superior to sample B. It is clear from this test that higher viscosity oils forms very durable thick protective layer on the metal surface.

We observed sample B protection is less due to dripping of oil as the sample B viscosity is less which affects the thickness of the film on metal samples. On the other hand sample A is having high viscosity and showed good protection against rust.

Sample – A, oil viscosity is lower at elevated temperature (at 100 Degree C) and high at room temperature (at 40 Dec C) which indicates thixotropic property. Practical application of viscous oil at room temperature is difficult. In order to increase application easiness, it is common practice to add volatile solvent to reduce the viscosity of oil or apply the oil in elevated temperature. Solvent added oil reduces protection against the rust. Sample – C oil is having added solvent to reduce the viscosity compare to sample -A. Sample C is having lower protection life compare to sample A, even base content is same.

Sample D oil is less viscosity oil with VCI additives. Sample D demonstrated superior resistance in humidity test & salt spray test compare to all the samples. The VCI additive products outperformed the all other samples during our tests. The evident long protection against atmospheric corrosion, particularly in closed environments, can be achieved using vapor-phase inhibitors (VPIs) with less viscous oil similar to sample D. We assigned highest ranking to the sample A which is having high viscosity and sample C&D is as moderate. We have assigned sample B ranking as low.

1.5 Lubricity

Four ball wear test conducted to understand the lubricity effect of all the samples. It is evident from the test results the thixotropic oil (Sample - A) has less lubricity characteristics than other sample – D, & C. Sample A is viscous oil compare sample – D, C. However, viscosity dropped when the load is applied and more scar formation observed indicating lower lubricity. Test results shows that medium viscous oil provides better lubricity. Rust preventive oil with thixotropic property may not give desired lubricity effect. Wear is having negative effect and is undesirable we have assigned ranking high for sample which is giving less wear and hence, the sample B as lowest and A is moderate. We have assigned ranking low for sample C & D.

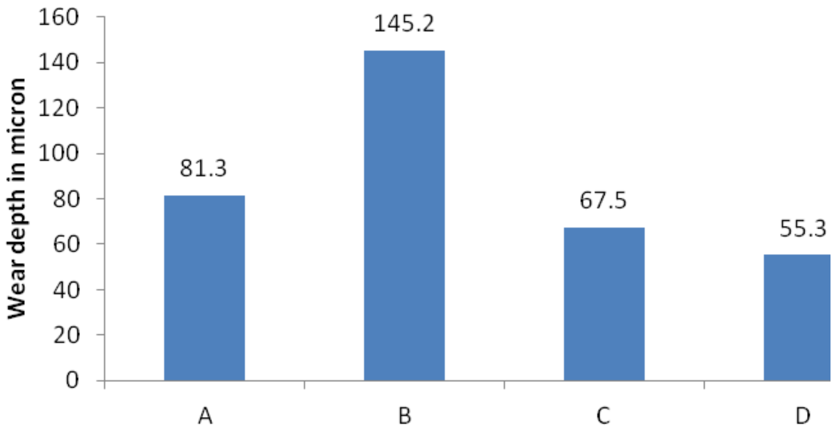

Fig 10. Avg wear depth

V. Observation Summary

Test results are summarized in the table 9.

Results are ranked as per pre-decided criteria and tabulation is furnished to arrive cumulative comparative ranking for samples. Maximum total score based on product of rank and weightage is considered as better RPO.

Table 9: Potential functional group of inhibitors present in the RPO's are mentioned below

Type test	Sample A			Sample B			Sample C			Sample D		
	Weightage in % (A)	Ranking (B)	Score (A*B)	Weightage in % (A)	Ranking (B) (B)	Score (A*B) (A*B)	Weightage in % (A)	Ranking (B) (B)	Score (A*B) (A*B)	Weightage in % (A)	Ranking (B) (B)	Score (A*B) (A*B)
Salt spray test	30	3	90	30	1	30	30	2	60	30	3	90
Humidity chamber test	40	3	120	40	1	40	40	2	80	40	3	120
Four ball test	10	2	20	10	1	10	10	3	30	10	3	30
Viscosity	15	3	45	15	1	15	15	2	30	15	2	30
Total	**275**			**95**			**200**			**270**		

Experiment results summary with score, we can clearly conclude that Sample D performed better in tests compare to other samples. Sample A and Sample C followed respectively to Sample D. It is clearly evident from summary of results that Sample B is poorly performing rust preventive oil.

It is clearly evident from experiments results rust preventive oils with VCI additives are having comparatively better rust protection. Sample D oil is mineral oil base carrier with amines and VCI additives having less viscosity. It is having better protective film formation capability and can sustain longer in environmental conditions. This oil is easy to apply as well with lesser viscosity. Better rust protection, better lubricity gives edge to this oil the application field.

Sample A also perform comparatively well in the testing. Sample A oil is mineral oil based carrier. It is having higher viscosity; due to thixotropic property lubricity property is not good. Formation of protective film is highly depending upon the application method because of higher viscosity of oil.

Combination of solvent with mineral oil and only solvent based carrier are not performing to the expectation based on test results. Sample C is comparatively better to Sample B as sample C contents combination of mineral oil with solvent based carrier. However, sample B is only solvent based carrier which performed poorly in the test.

VI. Conclusion

Based on our study, rust preventive oils with mineral oil based carrier provides better rust protection. Solvent based oils are having poor rust protection ability. Accelerated corrosion tests confirmed that either type of carrier or additives in the oil also impacts the rust protection ability of oil. Mineral oil with amorphous wax gives long protection than the solvent and solvent mixture type carriers. It can also be concluded that mineral oil with wax gives long protection; mineral oil which is having moderate viscosity with VCI additive gives superior protection.

Selection of suitable rust preventive oil for particular application is highly depending upon environmental conditions, protection period and also storage condition. However, based on this study, type of carrier and performance of rust preventive oil is having strong correlation.

Acknowledgements

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Glossary

Viscosity	Measurement of a fluid's resistance to flow. Which is defined as the force required moving a surface in area past a parallel surface at a speed.
VCI	A Vapor Corrosion Inhibitor (VCI) that prevents corrosion by covering parts with a protective atmosphere.
FTIR	Fourier Transform Infrared Spectroscopy. A test where infrared light absorption is used for assessing levels of soot, sulfates, oxidation, nitro-oxidation, glycol, fuel, and water contaminants

ASTM E2412	Standard Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry
ASTM D1748	Standard Test Method for Rust Protection by Metal Preservatives in the Humidity Cabinet
ASTM B117	Standard Practice for Operating Salt Spray (Fog) Apparatus
ASTM D4172	Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method)

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