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COMPARATIVE STUDIES ON THE PROPERTIES OF ADORCOAT - 950 TO THOSE OF COAT - 505 AS CORROSION INHIBITORS

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ABSTRACT

A study of the properties of a locally formulated corrosion inhibitor, Adorcoat–950 was carried out with that of the commercially available Coat-505, as well as crude oil. The t-test was used to statistically compare the average values of pH, density, specific gravity, pour point, flash point and viscosity at various temperatures. t-calculated for average pH in water and crude oil are 3.520 and 4.121 respectively while t-table value is 1.746. t-calculated values were found to be greater than t-table for all the parameters. Properties of Adorcoat-950 were found to be significantly different from those of Coat-505 as corrosion inhibitors at 95% confidence level.

KEYWORDS: Adorcoat-950, Coat-505, Corrosion inhibitor.

INTRODUCTION

The corrosion of metals and their alloys is a well-known environmental phenomenon. It affects metallurgical, chemical, oil and gas industries. It involves the gradual destruction of a material from the surface, leading to the loss of desirable physical, mechanical and aesthetic properties. The consequences of such action include tarnishing, loss of characteristic luster, poor performance and premature failure during application (Treseder, 1984). Corrosion leads to an increase in safety and environmental hazards as a result of structural collapse and the contamination of media by products of corrosion. In addition to these effects are the associated increase in shut-downs (interruptions in operation), increase in maintenance costs and ultimately in economic wastes (Cutler, 1980).

Corrosion inhibitors are very useful in the prevention and control of corrosion. The formulations used in the oil and gas production/transportation facilities, especially in pipelines often contain conventional organic film-type corrosion inhibitors. These include, the polymer-based types, which by themselves constitute a class of commercial importance as corrosion inhibitors. Such materials are starch, cellulose, rubber, polyethylene, etc. Studies on corrosion and corrosion inhibitors have constituted a major area of scientific investigation. The use of organic corrosion inhibitors to mitigate corrosion of steel rebar in concrete have been reported (Phanasgoankar et al, 1996; Phanasgoankar et al, 1997). Giddey et al (1998) reported the effect of increased temperature on the erosion-corrosion under turbulent conditions in Bayer Liquor. The effect of organic coating geometry on kinetics and mechanism of cut edge corrosion in organically coated galvanized steels have also been reported (Worsley and Powell, 1999). Scanning techniques for monitoring localized corrosion phenomena have been investigated (McMurray and Worsley, 1997; Worsley et al, 1997). Faltermeier (1998) reported a corrosion inhibitor test for copper-based artifacts.

Organic film-type corrosion inhibitors are generally easier and less complicated to use. Their handling presents no problems and are more versatile in their effects against corrosion than the inorganic types, which are rather more restricted in their applications (Treseder, 1984). The polymer-based corrosion inhibitors are high molecular weight compounds, which usually form heavier, more bulky films. These films are normally tougher, more durable and possibly more effective, especially for heavy duty applications, such as oil and gas production, transportation and storage facilities' corrosion inhibition. Coat – 505 is a commercially available polymer-based corrosion inhibitor suitable for this kind of application while Adorcoat – 950 is a locally formulated alternative by Gamor Chemical and Allied Limited, Port Harcourt.

A product formulation (such as a corrosion inhibitor) has to be characterized before use is initiated especially on a large or commercial scale (Ump, 1985). This paper reports a comparative study of the properties of Adorcoat – 950 with the commercially available Coat – 505. This is to determine the suitability of Adorcoat – 950 for large scale industrial application

EXPERIMENTAL

MATERIALS

The locally formulated polymer-based (cellulose-based) corrosion inhibitor – Adorcoat–950 was obtained from Gamor Chemical and Allied Limited, Port Harcourt, Rivers State. The organic, cationic amine compound used as reference – the commercially available corrosion inhibitor, Coat–505 was obtained from Shell Petroleum Development Company Limited, Port Harcourt, Nigeria. It is a product of NL Industries/Treating Chemicals of Houston, Texas, U.S.A. Medium export grade of crude oil used in this study was obtained from the Shell Petroleum Development Company Limited, Port Harcourt. All other reagents used are of laboratory grade.

METHOD

Properties of Adorcoat – 950, such as density, specific gravity, pH, viscosity, pour point and flash point were determined and compared with those of an effective, commercially available polymer-based corrosion inhibitor – Coat – 505 in order to determine its suitability for use as corrosion inhibitor.

Determination of Density and Specific Gravity

ASTM D-287:82 (ASTM, 1960) method was used. A clean, dry and empty pycnometer bottle was weighed at room temperature. It was then filled with distilled water and reweighed. This procedure was repeated three times after which an average value was taken for water. The same experimental procedure was carried out for Adorcoat – 950, Coat – 505 and crude oil respectively. Density values were

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calculated using the following equation (Emiliani, 1987):

$$\rho = \frac{m}{v} \quad \ldots\ldots (1)$$

where ρ = density, m = mass (g) and v = Volume (cm^3)

Test of Solubility

Mixtures 0.1 – 50%, of the test samples were prepared with water and crude oil as solvents respectively. 100 cm^3 of each solvent mixture was poured into a separatory funnel, shaken vigorously for 15 minutes and then allowed to stand for 1 hour. The respective mixtures were examined for signs of separation, miscibility, or dissolution after 1 hour.

Determination of pH

Different concentrations (0.0 – 100%) of each of the corrosion inhibitors in water and crude oil were prepared as test solution in 100ml beakers. The pH of the various test solutions were then determined at room temperature using Mettler Delta 340 pH meter, which had been previously calibrated using an acidic buffer solution.

Determination of Viscosity

Adorcoat – 950 and Coat – 505 were respectively introduced into a clean, dry and calibrated U-tube viscometer up to the mark. The set-up was secured by a holder and inserted in a thermostatically controlled oil bath (30°C) and allowed to equilibrate to the bath temperature. The equilibration temperature was recorded and the flow time subsequently determined with the aid of a Hanhart stopwatch. The Kinematic viscosity (cst) was calculated using the following equation (Dean, 1992):

$$KV = Ct \quad \ldots\ldots (2)$$

Where C = Calibration constant (cst s^{-1}), t = time(s).

Determination of Pour Point

ASTM D-97 method was used (ASTM, 1960) Adorcoat – 950 was poured into a clean and dry test jar to the mark. A thermometer with its cork was used to close the jar with the thermometer properly immersed in the test liquid. The jar with its content was warmed to 115°F on a water bath and allowed to cool to 90°F. The set up was placed in a pour point machine and allowed to cool slowly at a constant rate. The jar was carefully removed, wiped with clean towel and then tilted to observe if the liquid flowed at intervals of 50°F. At the point, the liquid remained frozen on tilting the jar, it was held in horizontal position for another 5 seconds in order to further observe the flow characteristics. The pour point is taken 5°F above the freezing point.

The procedure was repeated for Coat – 505 and Crude oil samples respectively.

Determination of Flash Point

ASTM – D1310 method was used (ASTM, 1960). The test liquids, Adorcoat – 950, Coat – 505 and Crude oil respectively were first cooled in a cooling bath at 50°F after which it was poured into the cup of the flash point tester, to the level mark indicated. A thermometer was put in position with the bulb immersed in the sample and the pilot flame lighted, adjusted and passed at a slow but uniform speed across the mouth of the cup and at regular intervals while the cup was being heated with a heater at a constant rate of 50°F per minute until a flash occurred.

The flash point, which is the temperature at which the test flame causes a distinct flash in the interior of the cup, was noted. The procedure was repeated three times for each sample and an average value taken.

RESULTS AND DISCUSSION

Results of density, specific gravity, solubility, pour point and flash point measurements at room temperature (30°C) are shown in Table 1. results of pH measurements are shown in Table 2, while results of viscosity measurements at various temperatures are shown in Table 3.

Where SD = standard deviation

The average values of pH measurements of Adorcoal-950 in water and crude oil as well as that of Coat-505 in water and crude oil were calculated using the equation (Ogugbuaja, 2000):

$$\overline{X} = \frac{\sum x_i}{n} \quad \text{--------} (3)$$

where $\overline{X}$ = average pH value

n = number of measurements taken

i = 1, 2, ---n.

Standard deviations of the measurements were also calculated using the following equation:

$$SD = \sqrt{\frac{\sum (x_i - x)^2}{n}} \quad \text{--------} (4)$$

Results are shown in Table 4. Standard Error (SE) of the measurements were calculated using the equation:

$$SE = \left[\frac{SD_1^2}{N_1} + \frac{SD_2^2}{N_2}\right]^{1/2} \quad \text{--------} (5)$$

where SD_1 = Standard deviation of Adorcoat-950 measurements

SD_2 = Standard deviation of Coat-505 measurements

N_1 = number of measurements taken for Adorcoat-950

N_2 = number of measurements taken for Coat-505

The t-calculated values for various parameters measured were obtained using the equation:

$$\text{t-calculated} = \frac{|\overline{X}_1 - \overline{X}_2|}{SE} \quad \text{--------} (6)$$

where $\overline{X}_1$ = average value for Adorcoat-950

$\overline{X}_2$ = average value for Coat-505

SE = standard error.

t-calculated values were compared with values in the t-distribution table at 95% confidence level and given degree of freedom determined using the equation:

Degree of Freedom = (N_1 + N_2) –2 --------(7)

Results are shown in Table 5.

Results in Table 1 show that the average densities of Adorcoat-950, Coat-505, Crude oil and water are 0.941g/cm^3, 1.044g/cm^3, 0.868g/cm^3 and 1.009g/cm^3, while average specific gravities are 0.933, 1.035, 0.860 and 1.000 respectively. This shows that the average density of Coat-505 is greater than the average density of Adorcoat-950. However, both were found to be denser than crude oil. Water was denser than Adorcoat-950 and slightly less dense than Coat-505. The implication is that both Adorcoat-950 and Coat-505

Table 1: Results of Average values of Density, Specific Gravity, Pour Point, Flash Point and Solubility Measurements.

Material	Average Density ± SD (g/cm^3)	Average Specific Gravity ± SD	Average Pour Point ± SD (°F)	Average Flash Point ± SD (°F)	Solubility in water ($50g/100cm^3$)	Solubility in Crude Oil ($50g/100cm^3$)
Adorcoat-950	0.941± 0.0008	0.933± 0.0005	10.4± 0.05	84.2± 0.05	Soluble	Soluble
Coat-505	1.044 ± 0.0005	1.035 ± 0.0005	19.4 ± 0.08	125.6 ± 0.05	Soluble	Insoluble

Table 2: Results of pH Measurements

Concentration Of Sample in Crude Oil/Water(%V/V)	pH of Adorcoat – 950 in Water	pH of Adorcoat – 950 in Crude Oil	pH of Coat – 505 in Water	pH of Coat – 505 in Crude Oil
0.0	7.04	9.71	7.04	9.71
0.1	7.58	9.62	8.36	9.70
0.5	7.60	9.61	8.42	9.70
1.0	7.63	9.07	8.91	9.70
5.0	7.81	8.88	9.28	9.70
10.0	7.99	8.78	9.35	9.69
20.0	8.16	8.55	9.35	9.69
50.0	8.30	8.43	9.50	9.68
100.0	8.41	8.41	9.66	9.68

Table 3: Results of Viscosity Measurements

Temperature (°C)	Viscosity of Adorcoat – 950 ± SD (cst)	Viscosity of Coat – 505 (cst) ± SD
30.0	34.70 ± 0.082	17.65 ± 0.005
50.6	10.74 ± 0.005	10.62 ± 0.005
78.2	5.86 ± 0.005	2.79 ± 0.005
90.5	5.40 ± 0.005	2.11 ± 0.005
120.5	5.10 ± 0.005	2.09 ± 0.008

Table 4: Results of Average pH of Adorcoat-950 and Coat-505 in Water and Crude Oil

Material	Average pH in water ± SD	Average pH in Crude Oil ± SD
Adorcoat-950	7.84 ± 0.40	9.01 ± 0.49
Coat-505	8.87 ± 0.78	9.69 ± 0.01

are expected to settle out of the crude oil and into the aqueous phase where they are required for action on application to an oil well, tank or pipeline.

However, results of statistical analyses (Table 5) show that the t-calculated for density and specific gravity were 206 and 255 respectively while t-table is 2.132. Since t-calculated is greater than t-table in both cases, there is a significant difference in the average values of density and specific gravity of Adorcoat-950 and Coat-505. Adorcoat-950 was found to be soluble in water and crude oil ($50g/100cm^3$) unlike Coat-505, which is soluble in water and insoluble in crude oil. Thus, Coat-505 has application to water-based systems only, while Adorcoat-950 is expected to have a wider application both to water and oil-based systems.

The pH of Adorcoat-950, Coat-505, crude oil and water were found to be 8.41, 9.67, 9.71 and 7.04 respectively. This shows that both Adorcoat-950 and Coat-505 are alkaline with Coat-505 being more alkaline. Their addition to water was found to cause an increase in pH, which increased as their concentrations in water increased as shown in Table 2. The crude oil sample had a pH of 9.71, which is greater than that of the corrosion inhibitors. Addition of the corrosion inhibitors to crude oil lowers its pH as shown in Table 2. However, a dispersion of Coat-505 in crude oil only caused a slight reduction in crude oil pH, compared to greater reduction in the case of Adorcoat-950. This is most likely due to the fact that Adorcoat-950 is soluble in crude oil to a certain degree as against Coat-505, which is insoluble in crude oil. However, the pH in both cases remained in the alkaline region as shown by the average pH values within the concentration range of 0 – 100% (v/v) investigated, which were 7.48, 8.87, 9.01 and 9.69 for Adorcoat-950 in water, Coat-505 in water, Adorcoat-950 in crude oil and Coat-505 in crude oil respectively. Increase in acidity favours increase in corrosion rate while decrease in acidity generally favours reduction in rate of corrosion (Traseder, 1984). Therefore, Adorcoat-950 and Coat-505 perform well in this regard although Coat-505 was observed to show better performance than Adorcoat-950 since it has a higher pH value. A comparison of the average pH values of Adorcoat-950 and Coat-505 for concentrations investigated showed that there is a significant difference between the average pH of Adorcoat-950 and Coat-505 in water and crude oil as solvents. This is because t-calculated for pH of samples in water and crude oil, which are 3.520 and 4.121 respectively are greater than t-table, which is 1.746 at 95% confidence level as shown in Table 5.

The average viscosities of Adorcoat-950 and Coat-505 at room temperature (30°C) was found to be 43.70 cst and 17.64 cst respectively. This shows that Adorcoat-950 is about twice as viscous as Coat-505. However, their viscosities dropped very drastically with increase in temperature and more critically above 50°C when it then leveled out virtually below 10 cst for both inhibitors. This trend is shown in Table 3. Viscosity and other rheological properties including the effect of temperature on them are very important factors in the application of an organic film-forming type corrosion inhibitor.

Table 5: Results of t-calculated and t-table for Adorcoat-950 and Coat-505 at 95% confidence level

Parameter	t-calculated	t-table at 95% confidence level
Average pH in water	3.520	1.746
Average pH in crude oil	4.121	1.746
Average density	206.0	2.132
Average specific gravity	255.0	2.132
Average pour point	165.4	2.132
Average flash point	1075	2.132
Average viscosity at 30^{0}C	361.2	2.132
Average viscosity at 50.6^{0}C	31.58	2.132
Average viscosity at 78.2^{0}C	807.9	2.132
Average viscosity at 90.5^{0}C	865.8	2.132
Average viscosity at 120.5^{0}C	507.9	2.132

Coat-505 and Adorcoat-950 whose suitability for this application are being compared, are usually preferred in the oilfield for building stable films. However, the viscosity should be low enough, at least below 50cst, for ease of pumping and transportation (Traseder, 1984). Viscosities of Adorcoat-950 and Coat-505 at room temperature fall below this value. However, the pumping pressure for Adorcoat-950 is expected to be higher than that of Coat-505 especially at room temperature, since Adorcoat-950 has higher average viscosity.

t-calculated for average viscosities of Adorcoat-950 and Coat-505 at 30^{0}C , 50.6^{0}C, 78.2^{0}C, 90.5^{0}C and 120.5^{0}C were found to be 361.2, 31.58, 807.9, 865.8 and 507.9 respectively. When compared to t-table, it was found that t-calculated is greater than t-table (2.132) in all the cases investigated. Therefore, there is a significant difference in the average viscosities of Adorcoat-950 and Coat-505 at these temperatures.

The average pour points of Adorcoat-950, Coat-505 and crude oil were found to be 10.4^{0}F (-12^{0}C), 19.4^{0}F (-7^{0}C) and 10.4 ^{0}F (-12 ^{0}C) respectively. The average pour point of Adorcoat-950 was found to be significantly different from that of Coat-505 since t-calculated (165.4) is greater than t-table (2.132) at 95% confidence level as shown in Table 5. However, average pour point of Adorcoat-950 was found to be the same with that of crude oil. This implies that Adorcoat-950 can be applied to crude oil production and transportation systems without fear of it freezing before the crude oil sample. Adorcoat-950 was found to be better than Coat-505 in this regard since its average pour point (10. 4^{0}F (-12 ^{0}C) is lower than that of Coat-505 (19.4 ^{0}F (-7 ^{0}C)).

Results of average flash point measurements for Adorcoat-950 and Coat-505 are shown in Table 1, while results of the statistical comparison of the averages are shown in Table 5. The average flash point of Adorcoat-950 was found to be 84.2 ^{0}F (29 ^{0}C) while that of Coat-505 was 125.6 ^{0}F (52 ^{0}C). Statistical comparison shows that the two averages are significantly different since t-calculated (1075) is greater than t-table (2.132). This shows that Adorcoat-950 has a very low flash point compared to that of Coat-505. The implication is that Adorcoat-950 is inflammable at ordinary temperature (29 ^{0}C) making it dangerous for application near any source of ignition.

CONCLUSION

The properties of Adorcoat-950 such as density, specific gravity, pH, viscosity, pour point and flash point were found to be significantly different from those of the commercially available corrosion inhibitor, Coat-505. On the basis of this result, Adorcoat-950 may not function exactly as Coat - 505 as corrosion inhibitors. Adorcoat-950 has a considerably low flash point and thus should be applied by squeeze or continuous injection at temperatures below 29^{0}C and away from any source of ignition.

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