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# STUDY OF THE INFLUENCE OF XYLENE-BASED CHEMICAL ADDITIVE ON CRUDE OIL FLOW PROPERTIES AND PARAFFIN DEPOSITION INHIBITION

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## ABSTRACT

**Paraffin related problem appears through out the production process of nearly all kinds of crude oils all over the world. It also appears in the dewatering process and the long distance crude oil transportation. In Nigeria, operators spend millions of dollars each year to control the deposition of paraffin and to deal with other sand related problems. Expenditures of this magnitude obviously have a significant impact on profits. This paper introduces the latest research and development of a novel chemical additive for the control of paraffin deposit and the successful application on Nigerian oilfields.**

**Results of cold spot and dynamic flow tests revealed the unique potential of the xylene-based formulation for achieving greater paraffin deposition efficiency, pour point depression and improved transport properties for a wide range of waxy hydrocarbon systems in comparison with other conventional paraffin deposit-control chemicals. The economic benefits and cost effectiveness of using this chemical for inhibiting wax deposition has been demonstrated in a field performance evaluation.**

## I. INTRODUCTION

There are many literatures (Shock, et. al. 1955; Mendell, and Jessen, 1970; McClaffin and Whitfill, 1984; Hsu, et. al., 1994; Azevedo and Teixeira, 2003; Adewusi, 1997; Adewusi, 1998; Garcia et. al., 1998; Hammami and Raines, 1999; Zhang, 1999; Garcia et. al., 2000; Garcia, 2001; Dong, et. al., 2001; Wang, et. al., 2003a; Wang, et. al., 2003b; Fasesan and Adewumi, 2003) reporting paraffin problems. These can be divided into two kinds. The first kind is mainly related to the research of mechanism of paraffin deposition and the set up of physical and mathematical models and also the development of softwares for analysis and anticipation of paraffin deposition potentiality for target oilfield; the second kind is specially concerned with a practical way of resolving paraffin deposition problem, such as mechanical, thermal, chemical, physical methods.

Paraffin deposition generally consists of wax, asphaltene, resin and sands, etc. The main component is wax. Wax is a solid state normal alkane with 15-80 carbon atoms and very few branch chains. Under the oil formation conditions, the wax dissolved in crude oil. But in the course of crude oil flowing through oil formation into the bottom hole of the well and then flowing up to the surface, because of decrease of pressure, temperature and the out come of gas, the wax is separated out to form crystals. The wax crystals will grow, aggregate and then precipitate on the wall of oil tube.

Paraffinic crude oils have been classified as into two structural categories, considering their molecular weight distribution, C24+ paraffins concentration and (n-/cyclo + isoparaffins) ratio. Also, different responses to commercial paraffin inhibitors were obtained by these two crude oil types, assessing the inefficiency of some paraffin inhibitors for crude rich in C24+ alkanes (Dong, et. al., 2001). It was demonstrated, through these previous studies that there is a complex interaction between crude oil fractions (especially paraffin classes distribution) and the tendency of the crude oil to precipitate wax. Usage of an effective paraffin inhibitor has a potential for significant savings versus removal procedures. Since paraffin characteristics and contents vary drastically from reservoir to reservoir, production problems and solutions also vary. Methods that are effective in one system are not always successful in others (Garcia, 2001).

There are many additives that have been tried in the field but none has economically solved the paraffin deposition and flow problems for extended periods of time due probably to the changing paraffin deposition tendencies of crude oil in response to changes in operational parameters. The study has therefore been carried out to address some of these limitations. The main goal of this work is the development and performance evaluation of a novel chemical additive for effective control of paraffin deposition from a wide range of waxy crudes and achieving greater pour point depression and improved transport properties for a wide range of waxy hydrocarbon systems in comparison with other conventional flow improvers.

## II. LABORATORY RESEARCH

### 1. The evaluation of Paraffin-Inhibition Efficiency

Three kinds of crude oils were adopted in the test of paraffin deposition that is Ebocha, Omon and Oso crude oils. Paraffin deposition tests and the relative efficiency of the promising chemical additive and commercially – available paraffin deposit–control chemicals were evaluated using cold spot and dynamic flow tests. The amounts of deposited paraffin with and without adding paraffin inhibitor were measured. Paraffin Inhibition Efficiency (PIE) was calculated according to the following formula:

$$PIE\ (\%) = 100\ \left(\frac{W_f - W_t}{W_f}\right)$$

where

$W_f$ - The reference amount of paraffin deposition without chemical treatment, g.
$W_t$ - The amount of paraffin deposition with chemical treatment, g.

### 2. Cold Spot Screening Tests

Figure 1 show the schematic diagram of the cold spot test apparatus. The apparatus consists of a ¼ -in O.D. soldered on the end of the cold finger. This assembly is immersed as shown in Fig. 1, in 250ml test (Ebocha crude) crude contained in a 300-ml beaker nested inside a 600-ml beaker. Ice-cold water at 6 $^0$C was circulated through the cold finger while water maintained at the desired test sample temperature(s) was circulated between the two nested beakers. The test sample was stirred by a magnetic stirrer and each test lasted for 60 minutes. At the end of each test, the plates were removed from the test sample and examined for the nature and amount of deposit. Several cold spot tests were conducted to screen individual chemical (methyl ethyl ketone (MEK), cyclohexanone, trichloroethylene and xylene) and their various combinations on the three available crude oils. For each test performed, measurements of the amount of deposits and transport properties (property and viscosity) of the test crude (with or without additive) were made. . Following this, the relative efficiency of the promising chemical additive and commercially – available paraffin deposit–control chemicals was evaluated using dynamic flow experiments.

### 3. Dynamic Flow Test

The purpose of the dynamic flow test was not to simulate exact field condition under which (wax) deposition occurs. This is because there were several parameters such as temperature and pressure gradients, fluid viscosity, oil column, phase changes, which can not be adequately simulated in the laboratory.

The approach employed in this test is to simulate sufficiently severe condition for deposition is a vertical assembly. This condition was then maintained throughout the length of each test.

### 4. Test Procedure

Figure 2 shows the simplified diagram of dynamic flow experimental set-up. The vertical test section is made of 3.1 mm thick Pyrex cylindrical glass, 12.5 mm I.D with an overall length of 61.0mm. The ice-cold environment surrounding the test section was maintained at close to $0^0$C to simulate severe condition for wax deposition process during the passage of the test crude. The cases considered are:

1. flowing the test crude from the wellbore until it reaches a particular level in the vertical test section, and maintaining this oil column for the entire period of wax deposition test (approximately one hour). This was meant to simulate a "dead well" condition which was due to severe problem of wax deposition.

2. continuous flowing of the test crude at $10cm^3/s$ from the wellbore through the test section to the top reservoir over the entire period of the test.

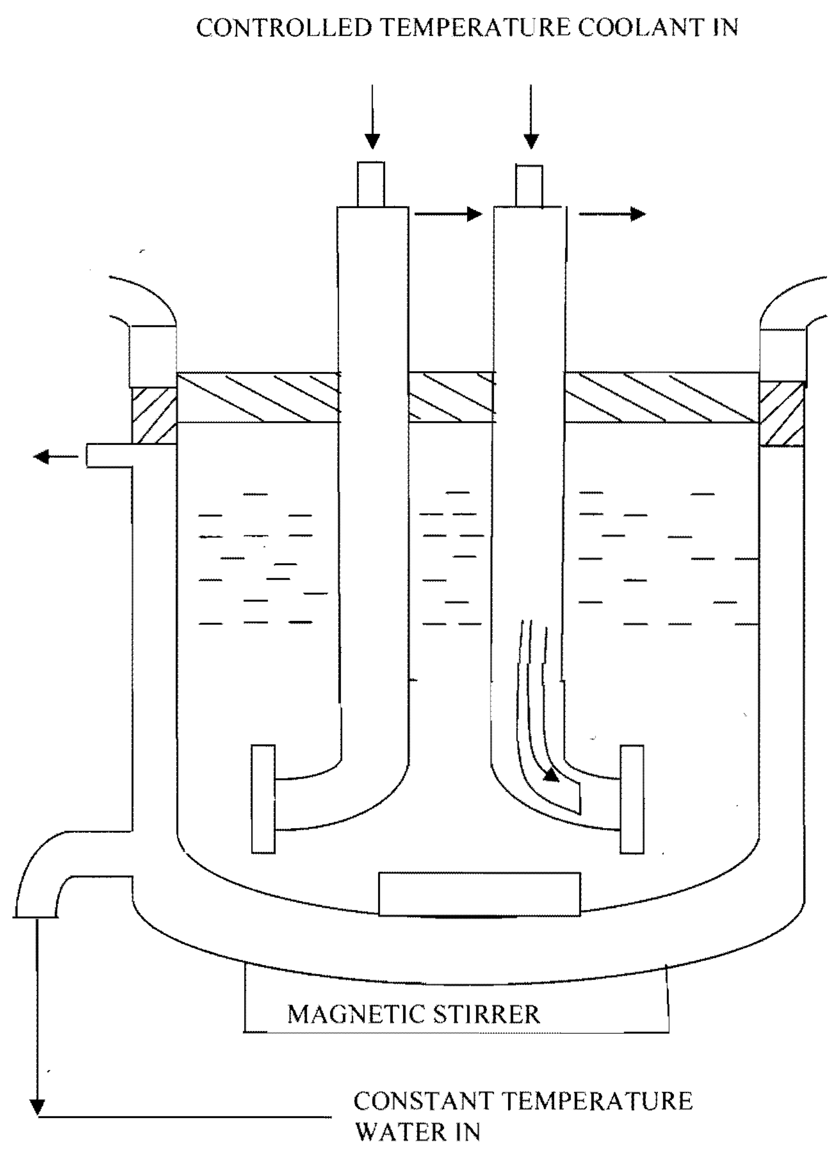


**Figure 1: Cold Spot Tester**

In order to evaluate the performance of the tested additives under the dynamic cases maintained in (1) and (2) above, two chemical injection modes were employed.

(a) in case (1) , the additive was injected from the top of the oil column to test the soaking ability and wax deposit dissolution power of the additive and hence simulate the case for the wellhead chemical treatment of a waxy "dead well".

(b) in case (2), additive was injected to the test crude before commencement of the crude flow through the vertical test section, to simulate downhole chemical treatment of wax deposit-prone producing well. For various tests conducted, additive-to-oil ratio of 0.01 was used and the difference between the weight-after – run and the weight–before-run of the test section gives the weight of wax deposited.

## 5. Field Application

The xylene-based paraffin deposit inhibitor (TEX) was field tested at Omoku-west 1 in September, 1996. Omoku-west 1 is one of the NAOC (Nigerian Agip Oil Company) installations with severe paraffin deposit problem. The chemical was injected from a designated point along the flow line of Omoku-west 1. Crude oil samples at both the upstream (near-well head) and downstream (manifold) locations of the injection point were carried out on daily basic for 12 days. The criteria used to evaluate the effectiveness of the injected chemical are the relative magnitude of the pour point, viscosity and API gravity of the produced crude before and after chemical treatment.

Also, tests of corrosiveness and compatibility of chemical with fresh water, DEA solution and demulsifier were conducted.

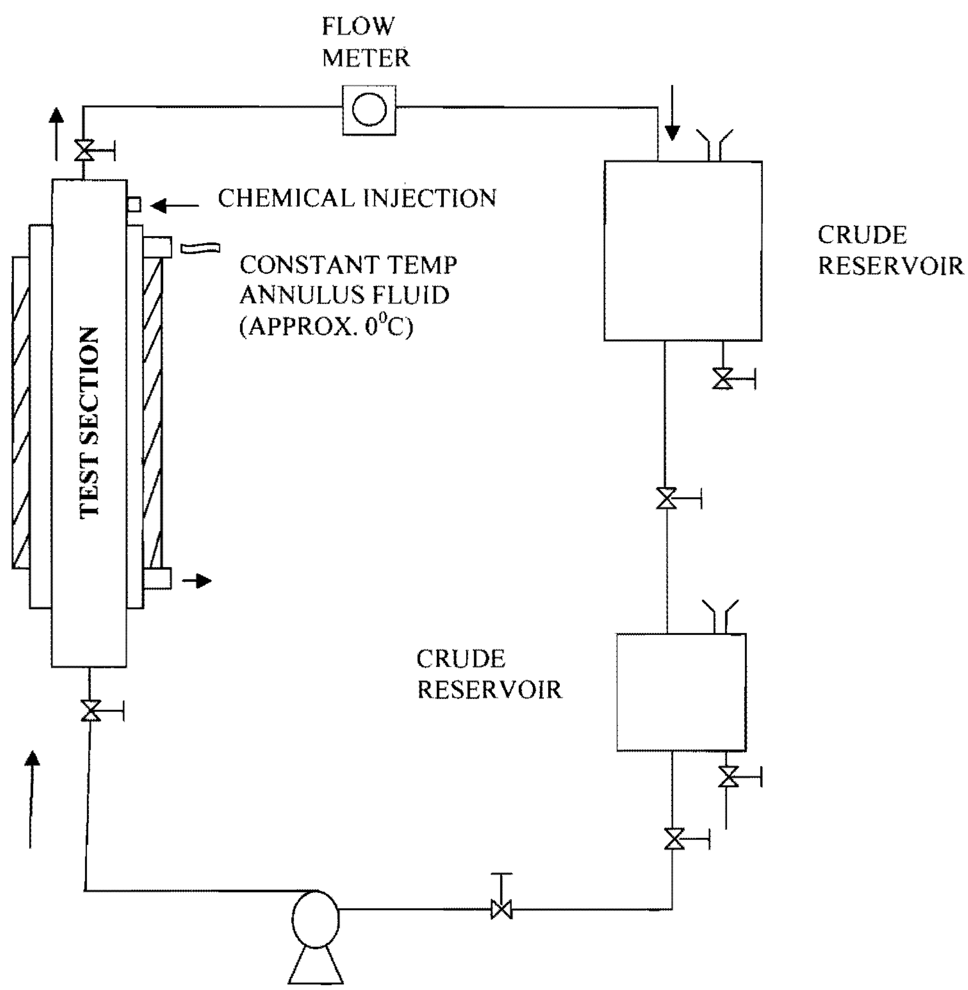


**Figure 2: Dynamic Flow Experimental Apparatus**

# III. RESULTS AND DISCUSSIONS

The discussion of the results is presented in three major parts, namely

(a) Chemical Screening Study
(b) Comparative additives' Performance Study
(c) Field Performance Study

## 1. Chemical Screening Study

Table 1 shows the results of the preliminary cold spot screening of the four main chemical considered. Several other chemicals (MIBK, MIPK, Acetone, butan-2-one, hexane and diethyl glycol), which were also tested but performed poorly and are therefore discarded.

The screening test result depicted by Figure 3 reveals that trichloroethylene display the highest wax deposition inhibiting capability and best pour point depressing property thus exhibiting the highest potential for reducing the waxing tendency of the test crude (Ebocha). Trichloroethylene is closely followed by xylene and cyclohexanone which MEK took the fourth position.

Based on this result, trichloroethylene was chosen as the root chemical for the intended chemical additive. Table 1 also contains test results for various combinations of trichloroethylene and the other three chemicals. The results are graphically displayed in Figure 4. The trends observed showed that trichloroethylene-xylene binary system performed most efficiently and was therefore chosen for further tests in order to optimize its performance.

In practice, the actual (optimum) injection requirement in the field would be determined on crude type and should be therefore be established during a field test.

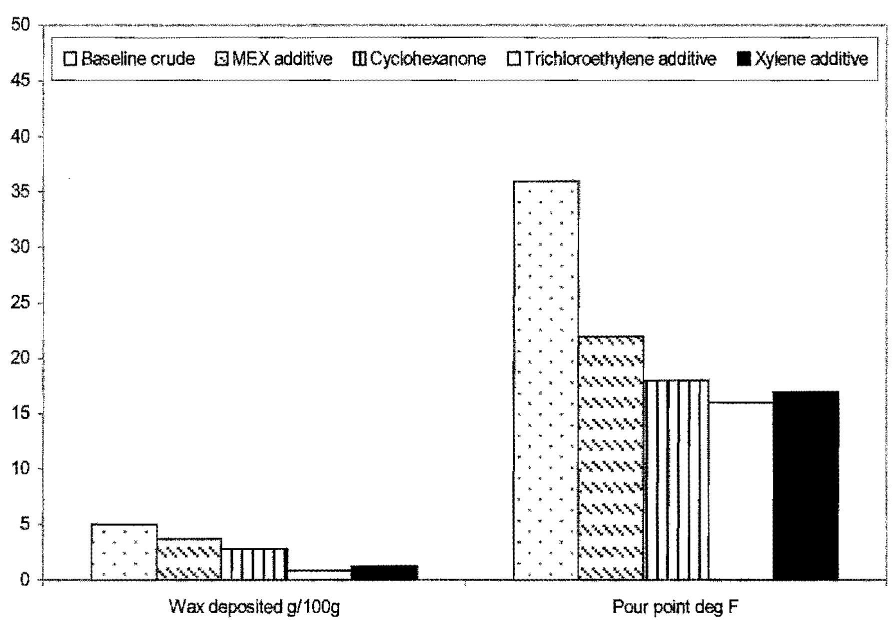


**Figure 3: Cold Spot Screening Tests of Chemical Additives on Ebocha Crude**

**Table 1: Cold Spot Test Data for Original samples and Blends of Binary Systems on Ebocha Crude (Additive/Crude Ratio = 0.01; Test Crude Temp. = 77 $^0$F)**

| Chemical additive | Paraffin Deposited from Test crude at 0 $^0$C g\|g | Pour point of crude-additive mixture $^0$F |
|---|---|---|
| No additive | 0.050 | 36 |
| Methyl ethyl ketone | 0.037 | 22 |
| Cyclohexanone | 0.028 | 18 |
| Trichloroethylene | 0.009 | 16 |
| Xylene | 0.013 | 17 |

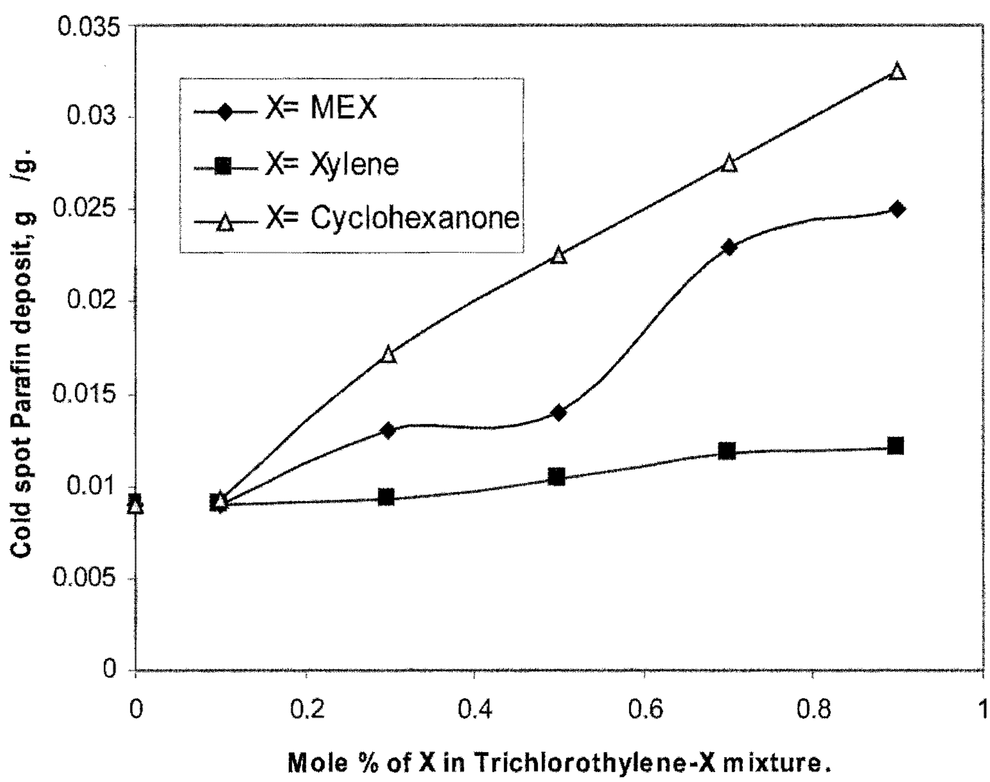


**Figure 4: Cold Spot Parafin Deposition Test of Trichloroethylene-Based Binary Systems**

### 1.1 Performance Optimization of Trichloro Ethylene–Xylene System

Optimal formulation of trichloroethylene-xylene binary system was considered in term of its composition and additive-to–crude ratio requirement. With respect to the former, Figure 5 show the dependence of additive's paraffin deposit inhibiting efficiency, pour point depressing capability and cost per drum (200 liters) on additive composition. A 50/50 (mole) binary system appears to be a reasonable option. This is because at this level the additive's efficiency is still fairly high while the cost is also reasonable comparatively.

Below the 50/50 (mole) level, that is, higher xylene concentration, the inhibitor efficiency decline significantly. Going above this level however, the observed increased in the efficiency is relatively small and this may not justify the additional cost requirement for field application. Consequently, the 50/50 composition level was considered to be optimal.

Figure 6 show the effect of additive-to-crude ratio on the performance of 50/50 trichloroethylene-xylene (TEX) binary system increasing level of additive/crude ratio produces and increase efficiency of TEX system. However, the differential increase in the additive efficiency showed a continuous decline. Furthermore, since multiple of chemical dosage to achieve less than 10% increase in the efficiency of the additive may not be justifiable from economic viewpoint; an additive/crude ratio of 1:100 has consequently been judged technically and economically to be a reasonable option.

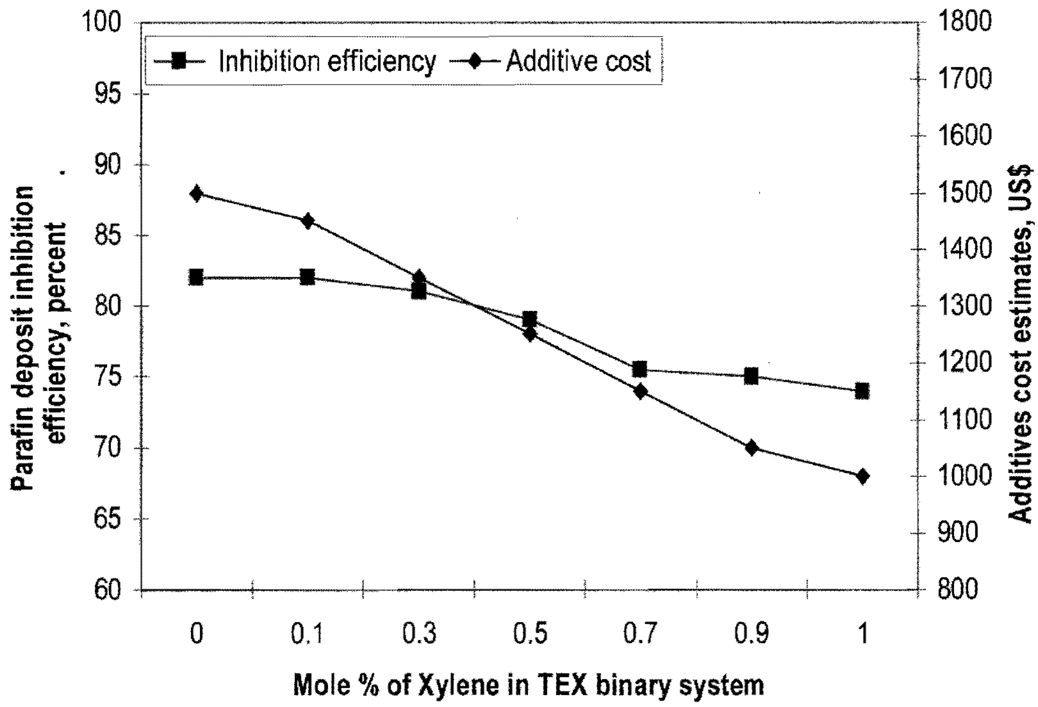


**Figure 5: Cold Spot Parafin Deposition Test of Trichloroethylene-Xylene (TEX) Binary**

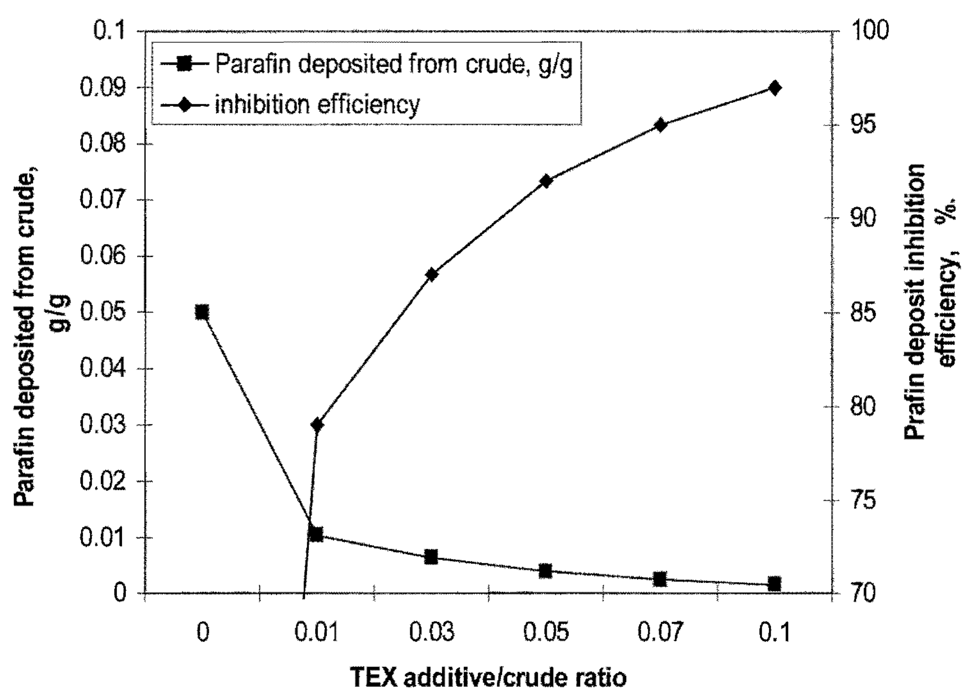


**Figure 6: Cold Spot Parafin Deposition Test of 50/50 TEX Binary System on Ebocha Crude**

## 2. Comparative Additives Performance Study

The performance of TEX additive was compared with three commercial anti-paraffin products currently being used by some major oil companies in Nigeria. The comparative tests were carried out using dynamic flow apparatus. For confidential reasons, the real identifies of the commercial products are not disclosed in this paper. They are referred to as AD1, AD2, and AD3 additives.

### 2.1 Static Oil Column Test Results

The results obtained when a waxy static oil column was treated with the four additives are presented graphically in Figure 7. Without the additive (baseline case) wax deposited by Ebocha, Omon and Oso crudes, respectively 0.16, 0.22 and 0.57 g/g. indicating that the Oso crude sample is waxier than the Ebocha and Omon crudes under the test condition.

The wax deposition from Ebocha crude was reduced to 0.06, 0.04, 0.03 and 0.02 g/g respective by AD1, AD2, AD3 and TEX additives. Significantly, this is equivalent to reduction in wax deposition potential of Ebocha crude from a scale of 100 to 37.5, 25, 17.6 and 13.6% respectively. Similarly, with the Oso crude test, AD1 exhibit the least efficiency followed by AD2 while AD3 and TEX displayed equally higher efficiencies, reducing the wax deposition from 0.57g/g to only 0.07g/g, an equivalent of deposition potential decrease of 87.7%. In contrast to the above trends, when Omon crude was treated, AD3 additive exhibited the poorest performance, giving less than 20% reduction in the wax deposition potential of Omon crude. With the use of A1, AD2 and TEX however, the wax deposition potential of Omon crude was substantially reduce to 45.5, 18.2 and 11.8 % respectively.

From the above results, TEX has consistently shown better performance in the treatment of a waxy static oil column than other commercial products tested.

### 2.2 Dynamic Flow Test Results

Figure 8 shows the results of the fully-developed dynamic flow tests. The base-line results give deposition rate of 0.142, 0.200 and 0.480 gram/min. For Ebocha, Omon and Oso crudes, their values were reduced respectively to 0.064, 0.090 and 0.20 gram/min by AD1 additive. The AD2 performed better in reducing the value to 0.008, 0.032 and 0.12 gram/min respectively. The AD3 also reduces the wax deposition rate to 0.04 and 0.009 gram/min in the case of Ebocha and Oso crudes but performed poorly with Omon crude. The overall best performance was exhibited by TEX with which no trace of wax deposit was observed in all cases. These results as previously observed for the static oil column test re-affirmed the superiority of the trichloroethylene-based (TEX) additives over the other three commercial anti-paraffin additives for controlling wax deposition from waxy crudes and gas-condensate.

Furthermore, information obtained from industrial source (Fagbemi, 1995) showed that the three commercial additives tested are more expensive than TEX (based on unit cost). Hence the trichloroethylene-xylene mixture developed in this study is potentially cost effective than these commercial products tested for inhibiting paraffin deposition in waxy oil wells.

## 3. Field Performance Test Result

### 3.1 Pour – Point Trends

Figure 9 gives the trends of the pour points of the untreated and chemically treated Omoku-west 1 (OW-I) crude. The plots showed that TEX has a depressing effect on the pour point and hence the waxing tendency of the crude. Comparison of the pour point of the chemically treated crude with the temperature condition of the downstream (manifold) sampling location showed that the fluid temperature is generally lower than the pour point of the crude (Figure 10); this condition may tend to promote wax deposition from the crude. The observed free flow pattern and the stabilized pressure condition and the downstream sampling location (Figure 11) however indicated no wax deposition. This must be due to excellent wax crystal modification properties of the product.

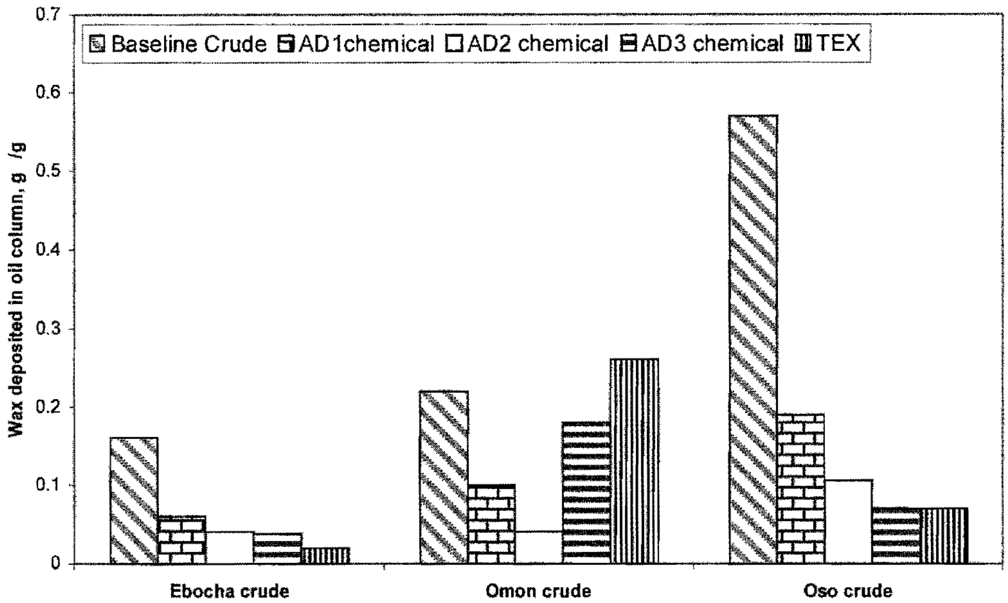


**Figure 7: Static Oil Column Wax Deposition Test of TEX and Chemical Products**

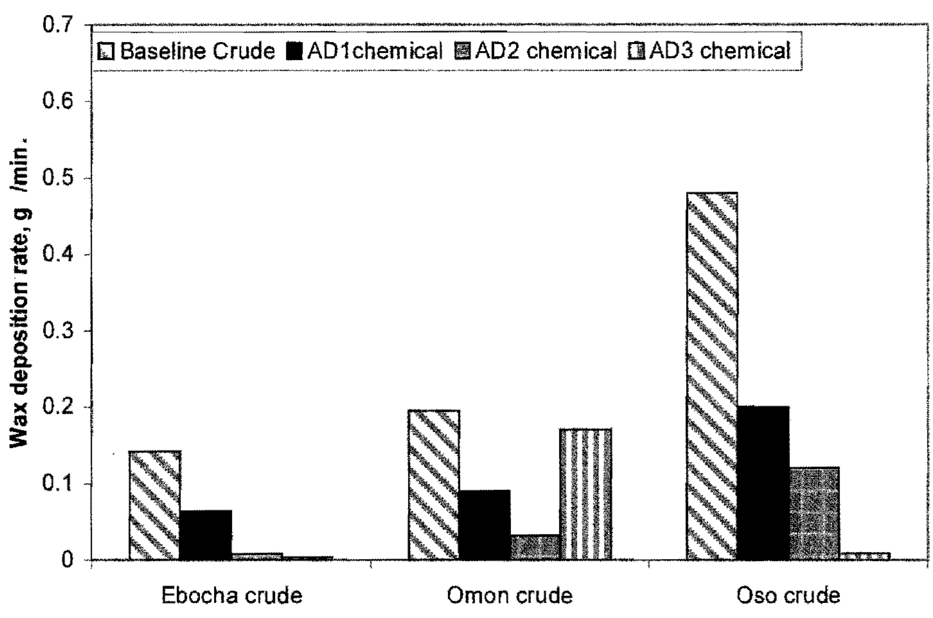


**Figure 8: Dynamic Flow Wax Deposition Test of TEX and Commercial Products**

TEX effect is not displayed in Figure 8 because no trace of wax deposit was observed in all cases.

### 3.2 Viscosity Trends

Figure 12 depicts the effect of TEX on the viscosity of OW- 1 crude. The trends showed a reducing effect indicating the ability of TEX to improve the flow characteristics of OW –1 crude under field condition in consistency with the static test results.

### 3.3 API gravity Trends

The API-gravity trends presented in Figure 13 showed that treatment of OW-1 crude with TEX caused significant increase in the crude's API-gravity over the 12 – days test period in consistency with the static test result. These increases are well over 2 degree reaching up to 6 or more in some days. These trends re-affirm the capability of the product to achieve improved flow characteristic of Omoku – west 1 crude.

Conclusively, judging from the pour point, viscosity and API-gravity observed for the field test, TEX has evidently demonstrated a good performance and great potential for inhibiting wax deposition and achieving improved flow characteristics of OW –1 crude at fairly low chemical dosage of less than 60ppm.

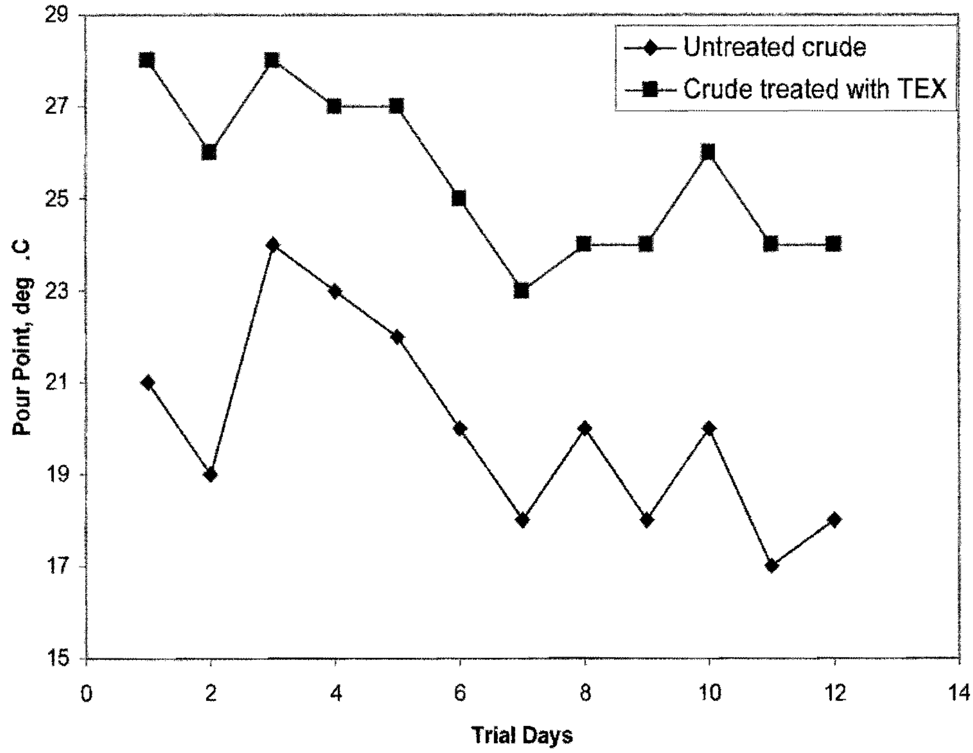


**Figure 9: Pour Point Trends of Omoku-West1 Crude**

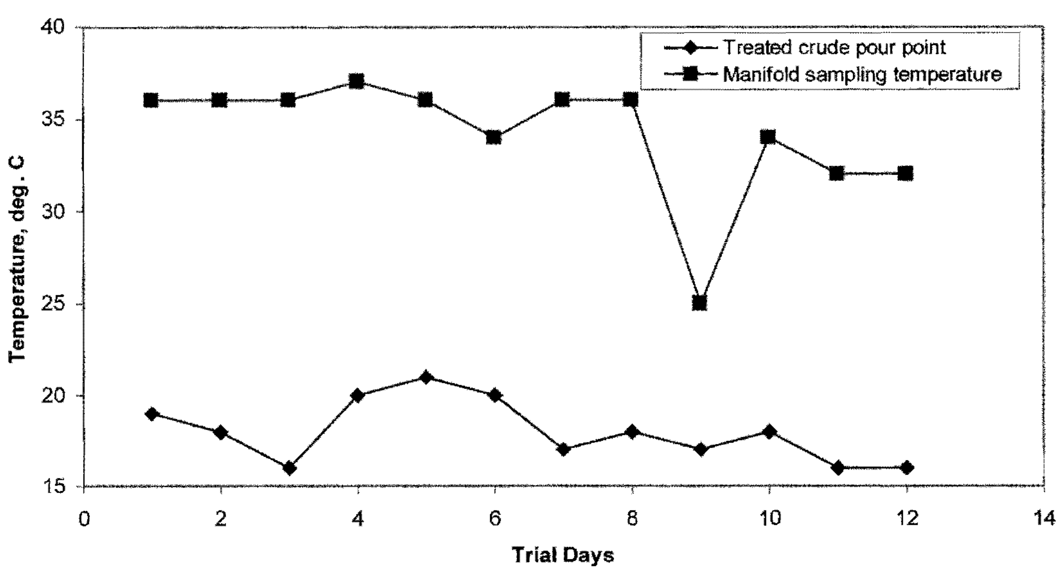


**Figure 10: Treated OW-1 Crude Pour Point and Manifold Sampling Temperature Trends**

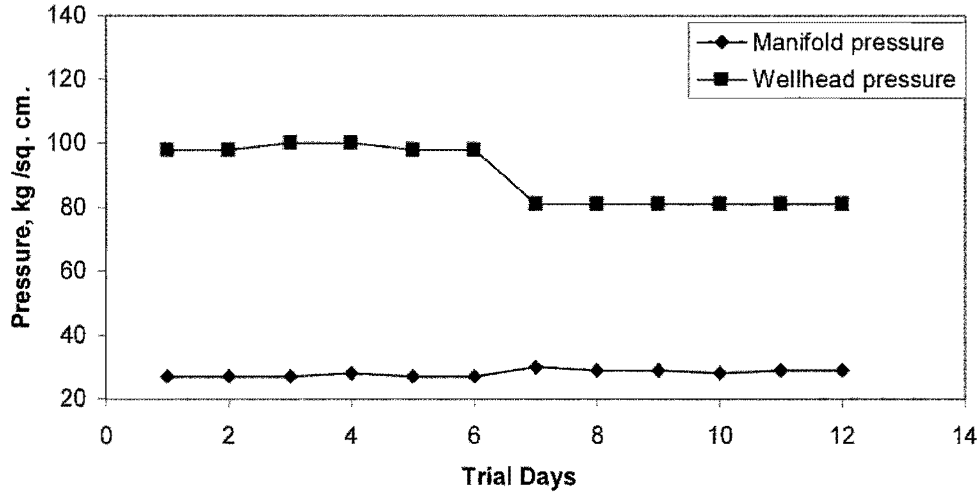


**Figure 11: Treated OW-1Crude and Manifold Sampling Pressure Trends**

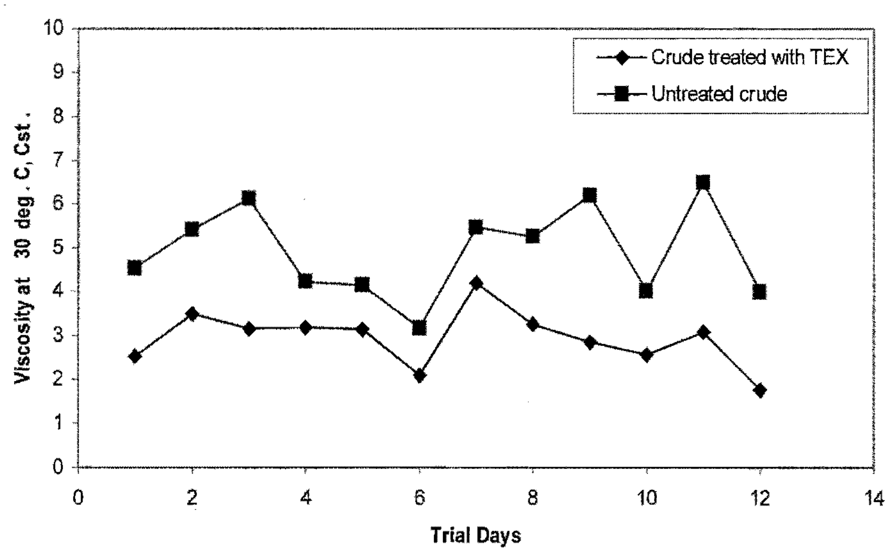


**Figure 12: Viscosity of OW-1Crude**

### 3.4 Corrosive Compatibility Test Result

The copper string corrosion test result on the product rules out corrosion behavior by giving a negative response. Table 2 provides a brief description of the observation made when TEX was contacted with fresh water, DEA solution (26%) and a demulsifier. It is observed that TEX is completely insoluble in water which will ensure that all chemical injected goes into oil phase where it is needed and also rules out the possibility of colloidal formation and foaming phenomenon commonly observed with other anti-paraffin chemicals. TEX also has no detrimental effect on the demulsifier.

**Table 2: Compatibility Test Results**

| Test with: | Observation with TEX additive |
|---|---|
| Fresh water | Two clearly defined immiscible layer of TEX on top with clean water at the bottom. No precipitate formed and no foaming indication. |
| DEA solution | Two immiscible phase emerged comprising an upper yellow layer and a colorless bottom phase |
| Demulsifier | A single black phase observed. The odour is predominantly that of demulsifier. |

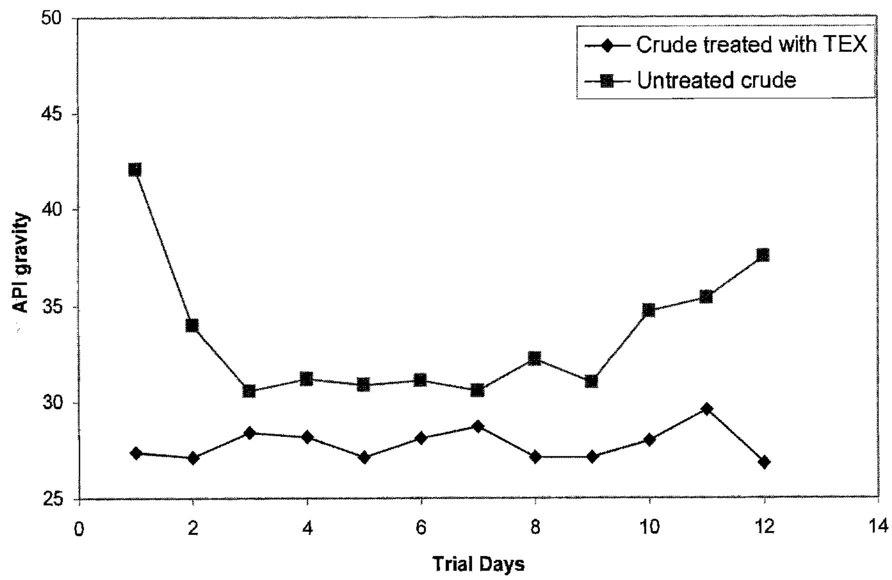


**Figure 13: API Gravity of Omoku-Westl Crude**

## IV. CONCLUSIONS

From the extensive laboratory and field tests carried out with various chemical combination and commercially available anti-paraffin chemicals, the following conclusions were drawn:

a. In the design of paraffin inhibitor's formula the first consideration, which needs to consider is the co-crystallization between inhibitor and wax aimed at inhibiting wax crystals aggregation and growing up; the second is the stable dispersion of wax crystals in the liquid hydrocarbon (crude oil); the third is the pour point depressing and viscosity reducing effects. These considerations can satisfactorily solve various paraffin deposition problems. Paraffin inhibitor, such as the trichloroethylene-xylene mixture (TEX) developed in this study is a successful example which formula is well designed according to the above principles.

b. Trichloroethylene-xylene mixture (TEX) has good effects of inhibiting paraffin deposition on the transfer pipelines for Ebocha, Omon and Oso crude oils. The formulation has a good viscosity-reducing effect for the tested crude oils. At the same time, it has synthetic functions of reducing pour point.

c. Performance comparison test of TEX and commercial ADl, AD2 and AD3 paraffin inhibiting chemicals using Ebocha, Omon and Oso crude oils revealed that TEX additive has a better application effect and tremendous economic benefit.

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