International Journal of Research Publication and Reviews

Effect and Remediation of Wax Precipitate on Petroleum Production Tubing for A Crude Oil Sample from The Niger Delta

Egonu Chiamaka and Engr. (Mrs) O. B Ajediti

Department Of Chemical/Petroleum Engineering, College Of Engineering, Afe Babalola University Ado-Ekiti, Nigeria.

ABSTRACT

Wax is one of the solid phases encountered in the production system. Wax depositions in production systems constitute a critical concern to crude exploration and production operations because it can build up in production equipment and pipelines, potentially restricting flow (reducing volume produced) and creating other production problems. The aim/ objective of this project work is to demonstrate the solubility of wax precipitate using different solvents (toluene, kerosene and diesel) and to determine the most economic solvent mix for dissolving wax precipitate in petroleum production tubing. The test on wax solubility was performed to determine the rate at which wax dissolves in these solvents, in order to select the most suitable solvent/solvent mixture for removing wax deposits in oil tubing. 5g of wax precipitate was dissolved in 100% Toluene, 100% Kerosene, 100% diesel, 90:10, 80:20, 70:30: 60:40, 50:50, 40:60, 30:70, 20:80 and 10:90 of Toluene : kerosene and Toluene: diesel mixtures respectively with time ranging from 30minutes to 150minutes. The result shows that 100% Toluene dissolved the precipitate within the shortest contact time (70mins).The 90:10 and 80:20 Toluene: kerosene mixtures both dissolved the precipitate through the same contact time (90mins). The 70: 30 Toluene: Kerosene mix dissolved the wax through the contact time of (120mins) but all other ratios of the Toluene: kerosene solvent mix including the Toluene: diesel solvent mix could not dissolve the wax within the stipulated time variation. From the result, 100% Toluene dissolved the wax within the shortest contact time (70mins) but for economic reasons, other solvent mix most especially the 90:10 and the 80:20 toluene: kerosene ratios can also achieve similar result within 90mins but the 80:20 Toluene: kerosene mix is recommended for wax remediation in petroleum production tubing because it is the least expensive among the two. Furthermore, work can be done on the addition of more solvents in a solvent mix in different ratios such as 10:40:50, 20:50:30 and so on, in order to determine the optimum solvent/solvent mix.

Keywords: Remediation, Wax Precipitate, Crude oil, Tubing, Niger Delta

INTRODUCTION

Paraffin wax is a hydrocarbon component which consists of mainly normal alkanes, varying amounts of condensed cycloalkanes, isoalkanes and a very low percentage of aromatic materials. .Its molecular weights are usually less than 450, and the viscosity at 210°F normally will be less than 6 cSt. Either needle or plate type structures are common. Paraffin are high-molecular-weight alkanes (C^{20+}) that can build up as deposits in the wellbore, in feed lines etc.It is the nature of many crude oils that they deposit waxy materials called "paraffin" which congeal at cooler temperatures or are so viscous that production is difficult. The presence of paraffin wax in crude oil has caused flow and mechanical problems while the oil is flowing from the wellbore through surface production tubing, facilities and trunk line to the crude oil terminal. Precise knowledge of the potential for and extent of wax deposition can be critical in the successful design and operation of hydrocarbon production systems. Temperature is observed to be the main factor that controls the saturation of paraffin wax in oil. The decrease of temperature will result in the appearance of wax crystals.

The precipitation of wax from petroleum fluids may give rise to a variety of problems well known within the petroleum industry. Such problems include:

- higher viscosity of the crude oil
- increased energy consumption for pumping
- decreased capacity
- changes in the composition of the fluid
- Increased power requirements and failure of facilities in petroleum industry.

BACKGROUND OF STUDY

Wax is a white or colourless soft solid derivable from petroleum, coal, or oil shale that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms. It is a flammable, whitish, translucent, waxy solid consisting of a mixture of saturated hydrocarbons, obtained by

distillation from petroleum or shale. It is solid at room temperature and begins to melt above approximately 37℃ ; its boiling point is >370℃ (698°F). Wax is one of the heavy organics found in crude oil, which is a complex mixture of hydrocarbons.

In chemistry, paraffin is used synonymously with alkane, indicating hydrocarbons with the general formula C_nH_{2n+2}. The name is derived from Latin parum ("barely") + affinis, meaning "lacking affinity" or "lacking reactivity" referring to paraffin's unreactive nature. The paraffin which deposits in various parts of a well is a carbonaceous material which is not soluble or dispersible by crude oil under the conditions where deposition occurs. These organic deposits can act as chokes within the wellbore, resulting in a gradual decrease in production with time as the deposits increase in thickness. This 'paraffin' normally consists of high molecular-weight paraffin hydrocarbons - both straight-chain and branched; resins and asphaltic materials of undetermined nature; occluded oil and water, and possibly sand and silt. This can result in producing problems unless some remedial action is taken on a systematic and periodic basis. Deposits can vary in consistency from soft accumulations to hard, brittle deposits. The deposits are firmer and harder as the molecular weight of the paraffin deposits increases. The primary cause of wax or paraffin deposition is simply a loss in solubility in the crude oil. This loss of solubility is usually a result of changes in temperature, pressure, or composition of the crude oil as a result of loss of dissolved gases. The ability of the crude oil to hold the paraffin in solution is generally quantified with two indicators: "pour point" and "cloud point".

When crude oil is cooled, the temperature at which wax crystals begin to separate from solution and a clear solution of hydrocarbons turns cloudy is called the "cloud point". The "pour point" is defined as the temperature at which the crude oil will no longer flow when tilted to a horizontal position in a bottle as a result of the forming of small wax crystals which form an interlocking network that supports the hydrocarbon liquid within it. The lighter components in crude oil keep the heavier components in solution. This solubility depends very strongly on the temperature. If the temperature of the oil is decreased, solubility of the heavy hydrocarbons may be sufficiently reduced to cause precipitation of these components in the form of solid wax crystals. The presence of wax crystals changes the flow behaviour of the crude oil from Newtonian to non-Newtonian. Furthermore, if the oil is cooled during transportation, the wax crystals tend to deposit on the colder pipe wall. Wax deposits can lead to increased pipeline roughness, reduced effective diameter, more frequent pigging requirement and potential blockage. If the deposits get too thick, they can reduce the capacity of the pipeline and cause problems during pigging.

As the temperature of the crude drops below a critical level or as the low-molecular-weight hydrocarbons vaporize, the dissolved waxes begin to form insoluble crystals. Temperature, pressure and composition play an important role in wax formation of which temperature is predominant. The deposition process involves two distinct stages: nucleation and growth. Nucleation is the forming of paraffin clusters of a critical size ("nuclei") that are stable in the hydrocarbon fluid. This insoluble wax itself tends to disperse in the crude. Wax deposition onto the production system ("growth") generally requires a "nucleating agent" such as asphaltenes and inorganic solids. Paraffin deposits will be harder, if longer-chain n-paraffin is present. Once the nuclei are formed and the temperature remains below WAT, the crystal growth process occurs as further molecules are laid down in laminar or plate-like structures. As the oil flows to the surface, there is generally a reduction of temperature, pressure and the amount of dissolved gases contained in the oil. This reduction of temperature and gas are factors which cause reduction in the solubility of the paraffin in the crude. Thus, the solubility of the paraffin may be exceeded as the crude containing paraffin rises to the surface and flows to storage tanks at ambient temperature and pressure. For a paraffin problem to exist, the solid must separate from solution, and it must stick to some surface. When wax separates from the solution, it does not necessarily deposit on the pore sands, or pipe walls. There must be other forces or mechanisms (Sadeghazad *et al.*, 1998). The most important mechanisms that cause the deposition of wax are the following:

I.　Molecular diffusion: the mechanism of molecular diffusion is the deposition mechanism occurring during production in which the oil temperature is well above the cloud point until the oil comes in contact with a cold surface, at that point, wax comes out of solution and adheres directly to the cold equipment.

II.　Shear deposition (Addison, 1984): shear deposition of precipitated wax crystals occurs after the oil has fallen below the cloud point, and the crystals are transported to the wall by the shearing of the oil at the surface of the tubing or flow line.

III.　Alternate coating and draining of the solid surface by the oil: when a solid surface is intermittently coated with oil, the film of oil left on the surface drains away until it is too thin. Its movement is too slow to carry the soft gummy wax particles in suspension (Reistle, 1932). These particles are firmly attached to the surface while the oil continues to drain away.

IV.　 High difference between surface and oil temperatures (colder surface): when the surface is much cooler than the oil, a thicker film of oil will remain after each coating because the oil is more viscous (Reistle, 1932). As a result, more wax particles will be deposited.

V.　Evaporation of lighter constituents: as the lighter hydrocarbon components vaporize from the coated oil, the concentration of wax goes up in the remaining oil and this causes additional deposition of wax.

VI.　Gravity deposition: experiments have indicated that the suspended paraffin particles were going to be settled down with time. This shows that paraffin are deposited with gravity force. Of course, it depends on the specific gravity of the solvent. Because the specific gravity of wax is only slightly greater than that of the oil, it remains suspended in the oil and is carried along with it.

Shear dispersion is the main mechanism of deposition for any situation where oil temperatures are below the cloud point. The deposition of paraffin by molecular diffusion can take place even when the crude is below its cloud point, that is, the mechanisms of molecular diffusion and shear deposition

Paraffin wax is mostly found as a white, odourless, tasteless, waxy solid with a typical melting point between about 46 and 68℃ (115 and 154°F). It is insoluble in water, but soluble in ether, benzene, and certain esters. It has a density of around 900kg/m^3.The heat of combustion of paraffin is 42 KJ/g

and it is unaffected by most common chemical reagents but burns readily. It is an effective neutron moderator and was used in James Chadwick's 1932 experiments to identify the neutron. Paraffin wax is an excellent material for storing heat, with a specific heat capacity of 2.14-2.9 $Jg^{-1}K^{-1}$(joules per gram kelvin) and a heat of fusion of 200-220Jg^{-1}. Wax expands considerably when it melts and this allows its use in wax thermostatic element thermostats for industrial, domestic and particularly, automobile purposes. Wax deposition is an important and serious problem that often occurs in oil production operations. It can occur in producing sands, well-bores, or in the surface transmission lines. Wax deposition is most likely to occur in the well bore and surface transmission lines. However, wax deposits in reservoir sands may result in serious production losses that are difficult to overcome. The most common cause of loss of solubility of the paraffin in the crude oil is a decrease in temperature, which may occur for a variety of reasons (Newberry *et. al.*, 1985):

i.   Gas expansion while lifting fluids to the surface

ii.   Evaporation of the lighter constituents of oil during the release of dissolved natural gas.

iii.   Cooling produced by the crude oil and associated gas expanding through the perforations.

iv.   Radiation of heat from the tubing to the surrounding formation induced by intrusion of water into or around the wellbore.

v.   The rapid loss in pressure as oil approaches the wellbore through the pores of the reservoir rock may cause wax deposition by both the cooling effect and the loss of light ends.

The effects of deposits in are:

i.   Unnatural production-rate declines in both flowing and pumping wells.

ii.   Reduction of the internal diameter of the pipelines and tubing, which can eventually plug it.

iii.   Increased surface roughness on the tubing wall which causes increased back pressure and reduced flow rate.

iv.   Stuffing box failures

v.   Extra power consumption

vi.   Increased wear on pumping equipment.

vii.   Accumulations that fill process vessels and storage tanks, leading to system upsets and labour/OPEX-intensive clean up and disposal problems.

viii. Interference with valve and instrumentation operation.

ix.   Increased risk of sticking pigs in the line and interference with the in-line inspection of flow lines and export lines by tools such as gauge pigs, calliper pigs and intelligent pigs.

Kerosene, also called paraffin or paraffin oil, is a flammable pale yellow or colourless oily liquid with a characteristic odour intermediate in volatility between gasoline and gas/diesel oil that distils between 125ᵒC (257◦F) and 260ᵒC (500ᵒF) (Gruse and Stevens, 1960). Kerosene is a crude-oil distillate similar to petro diesel but with a wider-fraction distillation. Kerosene was first manufactured in the 1850's from coal tar; hence the name coal oil as often applied to kerosene, but petroleum became the major source after 1859. From that time, the kerosene fraction was, and has remained, a distillation fraction of petroleum. However, the quantity and quality vary with the type of crude oil, and although some crude oils yield excellent kerosene quite simply, others produce kerosene that requires substantial refining. Chemically, kerosene is a mixture of hydrocarbons, and the constituents include n-dodecane (n-$C_{12}C_{26}$), alkyl benzenes, and naphthalene and its derivatives (ASTM D-1840). The chemical composition depends on its source and has a high number (>100,000) of isomers that are possible (Speight, 1999). The actual number of compounds in kerosene is much lower, and there are claims to less than 100 constituents but that again is source and process dependent. Acids can be present in kerosene aviation turbine fuels because of acid treatment during refining, but these trace acid quantities are undesirable because of the possibility of metal corrosion and impairment of the burning characteristics and other properties of the kerosene. Toluene is a colourless, flammable, non-corrosive liquid with a benzene-like odour. It is insoluble in water and soluble in acetone, absolute alcohol, ether, chloroform, benzene, petroleum ether, glacial acetic acid, and carbondisulfide (HSDB, 1991). Toluene occurs naturally at low levels in crude oil and is a by-product in the production of gasoline by a catalytic reformer or ethylene cracker. It is also a by-product of the production of coke from coal. Final separation and purification is done by distillation or solvent extraction processes used for BTX aromatics (benzene, toluene and xylene isomers). Toluene is widely used as an industrial feedstock and a solvent. In 2013, worldwide sales of toluene amounted to about 24.5 billion US-Dollars (Ceresana, 1990). Toluene reacts as a normal aromatic hydrocarbon in electrophilic aromatic substitution (Furniss *et al*., 1989). Because the methyl group has greater electron-releasing properties than a hydrogen atom in the same position, toluene is more reactive than benzene to electrophiles.

Diesel fuel is a mixture of hydrocarbons obtained by distillation of crude oil. The important properties which are used to characterize diesel fuel include cetane number (or cetane index), fuel volatility, density, viscosity, cold behaviour, and sulphur content. Diesel fuel specifications differ for various fuel grades and in different countries. Petroleum diesel, also called petro diesel, or fossil diesel is the most common type of diesel fuel. It is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule. Diesel fuel in general is any liquid fuel used in diesel engines, whose fuel ignition takes place, without any spark, as a result of compression of the inlet air mixture and then injection of fuel. Glow plugs, grid heaters and heater blocks help

achieve high temperatures for combustion during engine start up in cold weather. Diesel engines have found broad use as a result of higher thermodynamic efficiency and thus fuel efficiency. The most common type of diesel fuel is a specific fractional distillate of petroleum fuel oil, but alternatives that are not derived from petroleum, such as biodiesel, biomass to liquid (BTL) or gas to liquid (GTL) diesel, are increasingly being developed and adopted. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffin including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalene and alkylbenzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. Most diesel fuels freeze at common winter temperatures, while the temperatures greatly vary. Petro diesel typically freezes around temperatures of −8.1 °C (17.5 °F), whereas biodiesel freezes between temperatures of 2° to 15 °C (35° to 60 °F). The viscosity of diesel noticeably increases as the temperature decreases, changing it into a gel at temperatures of −19 °C (−2.2 °F) to −15 °C (5 °F), that cannot flow in fuel systems. Conventional diesel fuels vaporise at temperatures between 149 °C and 371 °C.

Paraffin wax depositions in production systems constitute a critical concern to crude exploration and production operations. Paraffin wax can build up in production equipment and pipelines, potentially restricting flow (reducing volume produced) and creating other problems. Recovery is impeded by accumulation of such waxy residues that tend to clog the pores of reservoir rock, well-casing perforations and screens, and tubing through which the oil flows. The unwanted effect of wax deposition could cause serious production impairment and other hazardous risk. Oil well paraffin treatments have been developed however that are designed to break down paraffin or asphaltenes and remove the build up from the well. This research is to demonstrate the effects and remediation of wax precipitate in different solvents (toluene, kerosene and diesel) with time variation.

LITERATURE REVIEW

There were early efforts to understand the nature of paraffin in petroleum production. In an early monograph, Mills (1923) reported that paraffin is generally made up of wax, oil, and up to 20% water (brine) and inorganic silt. While Bucaram (1967) found that paraffin waxes comprised 40 to 60% of a deposit in well tubing. Reistle and Blade (1932) remarked that the term 'paraffin' as used to describe this problem refers to the deposit of carbonaceous material which is not soluble or dispersible by the crude oil under the conditions where deposition occurs. The 'paraffin' normally consists of high molecular-weight paraffin hydrocarbons - both straight-chain and branched; resins and asphaltic materials of undetermined nature; occluded oil and water, and possibly sand and silt. In consistency, the deposit may vary from a soft, sticky material to one which is hard and brittle. Deposits are usually black, although lighter colours sometimes are observed. They further noted that deposits of crude wax or paraffin that accumulate in flow lines, in oil strings of wells, and on the face and in pores of the producing sand consist of very small wax crystals that tend to agglomerate and form granular particles of wax about the size of the grains of table salt. Deposited paraffin also contains gums, resins, asphaltic material, crude oil, sand, silt, and in many instances water, and vary in consistency from a mushy liquid to a firm hard wax, depending primarily upon the amount of oil present. Because oil gradually drains from the wax particles, the hardness of the paraffin deposit and the quantity of oil associated with the wax depends upon the length of time over which accumulation takes place, and the manner in which it was deposited. Wright, (1951) remarked that the number of different compounds and types of waxes found in paraffin are dependent upon the character of the crude oil. Oil is mostly mechanically trapped in the paraffin, held between wax grains. If a large amount of oil is present the paraffin tends to be soft, semi-fluid and more readily affected by heat. If very little oil is present, the paraffin is hard and less plastic; in this case an increase in temperature does not have much effect on the plasticity until the melting point of the wax is approached. Under the conditions of temperature, pressure and crude oil composition occurring in an underground reservoir, the paraffin is in solution in the crude. As the oil flows to the surface, there is generally a reduction of temperature, pressure, and the amount of dissolved gases contained in the oil. These reductions of temperature and gas breakout are the factors causing reduced solubility of the paraffin in the crude. Thus, as the crude containing paraffin rises to the surface and flows to storage tanks at ambient pressure and temperature, the solubility of the paraffin may be exceeded. Deposition tends to begin at the point in the system where the temperature of the system falls below its cloud point, and continues as long as there is a further drop in the solubility of paraffin in the crude. Solids deposition in production tubing, the most common example of the paraffin problem observed in production, is primarily a result of decreasing temperature, which causes a certain portion of the high molecular-weight fraction to precipitate (Weingarten *et al.,* 1988). Mechanisms other than decreasing temperature, such as pressure change, can reduce the carrying capacity of the solvent fraction of the reservoir fluid during transit from bottom hole to the surface. Pressure change resulting in liberation of volatile light ends as gas may prove to be a very significant mechanism in terms of its impact on overall recovery of oil and gas. The severity of the deposition as well as the location of the bulk of the deposition will depend on the amount of paraffin originally in the crude, the manner in which temperature and pressure of the crude are reduced, and other properties of the crude and of the paraffin. For a paraffin problem to exist, the solid must separate from solution, and it must stick to some surface. There are two main mechanisms of wax deposition: molecular diffusion, and shear deposition (Addison, 1984).

Gas chromatography provides compositional analysis of oil and wax. Simple paper chromatograms can provide useful information. These are carried out as follows: a drop of crude put on 2 by 3 inch blotting paper and allowed to spread to the maximum extent; then 2 to 5 drops of non-fluorescing naphtha added in the centre of paper and allowed to spread and dry; the result is viewed under ultraviolet light. This method may be useful if a large enough sample bases can be created and correlated with paraffin problems, and this information can be transferred to the field. Bucaram (1967) and Reistle and Blade (1932) among others used microscopic examination of oil after cooling below the cloud point. The shape and size of the crystals will give an indication of the expected paraffin problem. The precipitation of paraffin from a fluid does not necessarily lead to the accumulation of paraffin, because, often the paraffin crystals remained in and were produced with the crude (Brown (1940), Reistle and Blade (1932)). Once super saturation occurs, conditions favouring accumulations of paraffin are:

(1) Dead fluid spaces

(2) Rough places in pipe, such as grooves

(3) Cold spots, such as gas-lift foot valves

(4) Alternate coating and draining of pipe surfaces, as is normal in surging wells

(5) Oil produced as a mist, covering the pipe with a film, as is experienced in high gas-oil ratio wells

(6) Movement of oil at slow rates approaching streamline flow, (as in stripper wells) especially if the pipe is much cooler than the oil; in this case the paraffin may be precipitated directly on the pipe, and thus adhere to it; and

(7) The presence of foreign particles to provide nuclei for paraffin formation.

Paraffin accumulates in five locations in oil fields, they are:

i. Paraffin on the sand face or perforated liners. This is hard to detect, for the production decline is often mistaken for a normal decline. This condition is often present in old wells where a marked reduction in pressure has released light ends. Vacuum pumps may aggravate the situation.

ii. Paraffin in the tubing of flowing wells. The effects of deposit in tubing are abnormal production declines, complete killing of wells, and increased difficulty in running subsurface instruments, it is caused by the cooling from gas expansion and conduction of heat to the surrounding formation. The tendency of flowing wells to surge is one of the prime reasons for paraffin accumulation.

iii. Paraffin in pumps, sucker rods, tubing and wellhead of pumping wells. These deposits are caused by heat loss to wellbores and loss of volatile components. They produce increased wear on pumping equipment, increased power consumption, added difficulty in pulling rods, and failure of rods to fall; they also lead to production declines, rod failure and split tubing.

iv. Paraffin in flow lines. Caused by low temperatures in the flow lines. The effects are unnatural production-rate declines in both flowing and pumping wells, stuffing box failures, extra power consumption, and increased wear on pumping equipment.

v. Paraffin in stock tanks. For a long time it was not economical to recover the waxy ends for pipeline sale. Bottoms were used as lease road-surfacing material, or burnt in pits. Currently the expense of treating bottoms and the resultant high paraffin crude lead to lower profits.

MATERIALS AND METHODS

Materials

The apparatus and materials include:

I. Electronic Stirrer(Hamilton Beach Mixer)

II. Whatman 934-Ah Glass Microfiber Filter paper

III. Stopwatch

IV. Buchner funnel

V. Weighing balance

VI. Beaker

VII. 50ml density bottle (Pycnometer) with stopper

VIII. Measuring Cylinder

IX. Rheometer

X. Heater

XI. Petroleum Ether

XII. Distilled Water

XIII. Crude oil

Properties Measured

Various properties of the crude oil were measured and they include density, viscosity, pour point, cloud point, flash point.

Methodology

Density

i.   To obtain a clean and dry pycnometer, the pycnometer was rinsed with distilled water and dried with a small amount of acetone.

ii.   The dry and empty bottle with stopper was weighed on the weighing balance and the value was recorded.

iii.   The pycnometer was filled fully with water, the stopper was inserted and air bubbles were removed by tapping both sides of the bottle.

iv.   The full pycnometer with water was weighed on the weighing balance after drying the sides to get the weight of water.

v.   The pycnometer was filled to the brim with crude oil and air bubbles were allowed to rise before inserting the stopper, the pycnometer was afterwards weighed on the weighing balance.

Figure 1: Measurement of density using a Pycnometer

Viscosity

i.   The crude oil was heated in a heater and the temperature was checked constantly using the thermometer till it was slightly above 65°C.

ii.   At above 65°C, it was fixed in a rheometer and set to rotate at 150RPM.

iii.   As the temperature reduces to 65°C, the corresponding viscosity was checked and recorded also at 45°C.

Pour point and cloud point

i.   The crude oil was heated, poured in a clean dry test tube to a required minimum level and covered with a cork.

ii.   A Mercury in glass thermometer was inserted into the middle of the cork till it touches the crude oil in the tube.

iii.   It was kept in a refrigerator, and the temperature was checked every 5minute until it forms a cloudy appearance, the temperature was recorded at this point.

iv.   Checking of the test tube continued in the same manner until the temperature reaches a point at which the sample in the test tube does not show any movement for at least 5secs when brought to the horizontal position, this temperature is checked and recorded.

Figure 2: Measurement of pour point and cloud point

Flash Point

1. The brass cup was cleaned and dried.

2. The cup was filled with the sample exactly to the mark inside the cup and the micro flame was adjusted.

3. The cup was heated slowly at a controlled rate of 3°C per minute.

4. The micro flame was passed across the cup for every rise of 3°C.

5. The lowest temperature at which the flame flash is observed at any point over the liquid was recorded.

Precautions

i. The stopper number was to ensure that the stopper was not exchanged from bottle to bottle, since each stopper is ground to fit one bottle and no other.

ii. It was ensured that the pycnometer was clean and dry before the initial weighing.

iii. It was ensured that the pycnometer was held by the neck to avoid expansion due to heat of the hand.

iv. The capillary stopper was slowly inserted to prevent spilling the sample.

v. It was ensured that there were no air bubbles in the pycnometer and no air space at the top of the capillary because the air bubbles were allowed to rise to the top before inserting the stopper.

vi. Before weighing the full pycnometer, it was ensured that the outside was perfectly dry.

Wax precipitation

Wax precipitation is done using Juan et al (2009) method which is the modification of the method proposed by Burger et al (1981).

Procedures

i. The 40g of crude oil is dissolved in 40ml of petroleum ether and stirred for 30min using the electronic stirrer.

Figure 3: Crude oil being stirred By Electronic stirrer.

ii. The anti-solvent (3:1 acetone/n-pentane ratio) which is equivalent to 300ml: 100ml is added to the mixture and cooled to 253K (-20°C) for 24hrs in a refrigerator.

iii. Thereafter the solid phase present in the oil is separated by filtration in a Buchner funnel using a Whatman 934-Ah glass microfiber filter paper.

Figure 4: Separation of solid phase using a Buchner Funnel

iv. The precipitate is re-dissolved in n-hexane to separate the asphaltenes, and finally, the wax is weighed after solvent evaporation.

Precautions

i. I ensured weighing the sample after mixture with each solvent to get exact values for my calculation.

ii. Correct measurement of the solvent was ensured.

Wax solubility test

This test on wax solubility is performed to determine the rate at which wax dissolves in these solvents in order to select the most suitable solvent for removing wax deposits in oil tubing.

Methodology

    i.   5g of the precipitate wax was added to 40ml 100% toluene solvent in a conical flask and left to stand for 30mins without swaying or stirring it.

    ii.   An empty filter paper was weighed using a weighing balance.

    iii.   After 30minutes, the solution was filtered through a filter paper and was dried at constant temperature of 25°C after which the weight of the wax residue and the filter paper was taken, and the weight of the filter paper was deducted from it to determine the weight of the wax residue.

    iv.   The amount of wax soluble in the solvent was determined by subtracting the amount of the insoluble wax from the 5g initially added to the solvent.

    v.   The insoluble wax was dried and added to the solvent again, the same procedure was repeated for t= 50, 70, 90,120 and 150minutes.

    vi.   Step I-V was repeated for 40ml 100% kerosene, 100% diesel, 10:90, 20:80,30:70,40:60,50:50,60:40,70:30,80:20 and 90:10 of toluene-kerosene and toluene-diesel solvent mixtures respectively.

Precautions

    i.   The waxy residue and filter paper were dried after each filtration before weighing.

    ii.   The stopwatch was stopped in time to get accurate measurement of the soluble and insoluble wax at each particular time duration.

RESULT AND DISCUSSION

Result

Crude Oil Density

Table 1: Table of values of crude oil

	Weight (g)
Empty pycnometer (x)	22.25
Pycnometer + water (y)	71.12
Pycnometer + crude oil (z)	63.43

Weight of water = y-x = 71.12-22.25 = 48.87g

Weight of oil = z-x = 63.43-22.25 = 41.18g

Specific gravity or Relative Density (R.D) $= \frac{weight\ of\ fluid}{weight\ of\ water} = \frac{z-x}{y-x}$

Density = Relative Density x Density of water

Note:

Density of water = 1000kg/m^3 or 1g/cm^3

CALCULATIONS:

Relative Density (R.D)$=\frac{Z-X}{Y-X} = \frac{63.43-22.25}{71.12-22.25}$

$$R.D = \frac{41.18}{48.87} = 0.8426$$

$$\therefore R.D = 0.8426$$

Density = R.D X Density of water

Density = 0.8426 x $\frac{1g}{cm^3}$ = 0.8426g/cm^3

°API gravity $= \frac{141.5}{\gamma_o} - 131.5$

Since R.D = $\gamma_o = 0.8426$

°API gravity $= \frac{141.5}{0.8426} - 131.5 = 36.43$

°API gravity = 36.43 ≅ 36

Crude Oil Viscosity

Table 2: Table of values of crude oil viscosity taken at different temperatures

Temperature (ºC)	Viscosity (cp)
65	84.4
45	112.5

Pour point, Cloud point and flash point

Table 3: Table of Values for Pour point, Cloud point and Flash point

	Temperature
Pour point	8ºC
Cloud point	18ºC
Flash point	82ºC

Wax Solubility

Table 4: Values for Soluble Wax and Wax Residue for Toluene-Kerosene Solvent Mix.

Time		100% Toluene	100% Kerosene	90:10 T:K	80:20 T:K	70:30 T:K	60:40 T:K	50:50 T:K	40:60 T:K	30:70 T:K	20:80 T:K	10:90 T:K
Weight of Filter paper (FP) = 0.79 (g)												
30 mins	FP+ wax prep.	2.24	4.60	2.38	2.47	2.55	2.79	2,81	3.07	4.1	3.39	4.15
	Wax residue	1.45	3.81	1.59	1.68	1.76	2.00	2.02	2.28	3.31	2.60	3.36
	Soluble wax	3.55	1.19	3.42	3.32	3.24	3.00	2.98	2.72	1.69	2.40	1.64
50 mins	FP + wax prep.	1.02	3.37	1.27	1.47	1.59	1.59	1.66	1.81	2.20	2.14	3.84
	Wax residue	0.23	2.58	0.48	0.68	0.80	0.80	0.87	1.02	1.41	1.35	3.05
	Soluble wax	4.77	2.42	4.52	4.32	4.20	4.20	4.13	3.98	3.59	3.65	1.95
70 mins	FP + wax prep.	0.79	1.90	1.02	1.29	1.39	1.40	1.74	1.67	1.54	1.89	3.74
	Wax residue	0.00	1.11	0.23	0.50	0.60	0.61	0.95	0.88	0.75	1.10	2.95
	Soluble wax	5.00	3.89	4.77	4.50	4.40	4.39	4.05	4.12	4.25	3.90	2.05
90 mins	FP + wax prep.	-	1.57	0.79	0.79	1.00	1.26	1.31	1.48	1.49	1.63	3.15
	Wax residue	-	0.78	0.00	0.00	0.21	0.47	0.52	0.70	0.70	0.84	2.36
	Soluble wax	-	4.22	5.00	5.00	4.79	4.53	4.48	4.30	4.03	4.16	2.64
120 mins	FP + wax prep.	-	0.98	-	-	0.79	1.07	1.19	1.26	1.29	1.39	2.81
	Wax residue	-	0.19	-	-	0.00	0.28	0.40	0.47	0.50	0.60	2.02
	Soluble wax	-	4.81	-	-	5.00	4.72	4.60	4.53	4.5	4.40	2.98
150 mins	FP + wax prep.	-	0.79	-	-	-	0.87	0.93	1.09	1.19	1.14	2.63
	Wax residue	-	0.00	-	-	-	0.08	0.14	0.30	0.40	0.41	1.84
	Soluble wax	-	5.00	-	-	-	4.92	4.86	4.70	4.60	4.59	3.16

Table 5: Values for Soluble Wax and Wax Residue for Toluene-Diesel Solvent Mix.

Time		100% Toluene	100% Diesel	90:10 T: D	80:20 T: D	70:30 T: D	60:40 T: D	50:50 T: D	40:60 T: D	30:70 T: D	20:80 T: D	10:90 T: D
Weight of Filter paper (FP) = 0.79 (g)												
30 mins	FP + wax prep.	2.32	4.85	2.49	2.87	2.89	3.38	3.40	3.78	4.40	4.44	4.63
	Wax residue	1.53	4.06	1.70	2.08	2.10	2.59	2.61	2.99	3.61	3.65	3.84
	Soluble wax	3.47	0.94	3.30	2.92	2.90	2.41	2.39	2.01	1.39	1.35	1.16
50 mins	FP + wax prep.	1.00	3.90	2.18	2.59	2.60	3.22	3.24	3.56	3.58	4.31	4.52
	Wax residue	0.21	3.11	1.39	1.80	1.81	2.43	2.45	2.77	2.79	3.52	3.73
	Soluble wax	4.79	1.89	3.61	3.20	3.19	2.57	2.55	2.23	2.21	1.48	1.27
70 mins	FP + wax prep.	0.79	2.88	1.99	2.40	2.44	3.14	3.14	3.48	3.49	4.22	4,47
	Wax residue	0.00	2.09	1.20	1.61	1.65	2.35	2.35	2.69	2.70	3.43	3.68
	Soluble wax	5.00	2.91	3.80	3.39	3.35	2.65	2.65	2.31	2.30	1.57	1.32
90 mins	FP + wax prep	-	2.76	1.78	2.18	2.19	3.09	3.14	3.31	3.38	4.16	4.49
	Wax residue	-	1.97	0.99	1,39	1.40	2.30	2.35	2.52	2.59	3.37	0.70
	Soluble wax	-	3.03	4.01	3.62	3.60	2.70	2.65	2.49	2.41	1.63	1.39
120 mins	FP + wax prep.	-	2.52	1.58	1.97	1.98	2.90	2.92	3.19	3.24	4.05	4.29
	Wax residue	-	1.73	0.79	1.18	1.19	2.11	2.13	2.40	2.45	3.26	3.50
	Soluble wax	-	4.27	4.21	3.82	3.81	2.89	2.87	2.60	2.55	1.74	1.50
150 mins	FP + wax prep	-	2.36	1.33	1.79	1.84	2.78	2.79	3.03	3.04	3.91	4.18
	Wax residue	-	1.57	0.54	1.00	1.05	1.99	2.00	2.24	2.25	3.12	3.39
	Soluble wax	-	3.43	4.46	4.00	3.95	3.01	3.00	2.76	2.75	1.88	1.61

Table 6: % Solubility for Toluene-Kerosene Solvent mix

Time	100% Toluene	100% Kerosene	90:10 T:K (%)	80:20 T:K (%)	70:30 T:K (%)	60:40 T:K (%)	50:50 T:K	40:60 T:K	30:70 T:K	20:80 T:K	10:90 T:K
30mins	71	23.8	68.4	66.4	64.8	60	59.6	54.4	33.8	48	32.8
50mins	95.4	48.4	90.4	86.4	84	84	82.6	79.6	71.8	73	39
70mins	100	77.8	95.4	90	88	87.8	81	82.4	85	78	41
90mins		84.4	100	100	95.8	90.6	89.6	86	86	83.2	52.8
120mins		96.2			100	94.4	92	90.6	90	88	59.6
150mins		100				98.4	97.2	94	92	91.8	63.2

Table 7: % Solubility for Toluene-Diesel Solvent mix

Time	100% Toluene	100% Diesel	90:10 T: D (%)	80:20 T: D (%)	70:30 T: D (%)	60:40 T: D (%)	50:50 T: D (%)	40:60 T :D (%)	30:70 T: D (%)	20:80 T: D (%)	10:90 T: D (%)
30mins	69.4	18.8	66	58.4	58	48.2	47.8	40.2	27.8	27	23.2
50mins	95.8	37.8	72.2	64	63.8	51.4	51	44.6	44.2	29.6	25.4
70mins	100	40	76	67.8	67	53	53	46.2	46	31.4	26.4
90mins		50.6	80.2	72.4	72	54	53	49.8	48.2	32.6	27.8
120mins		65.4	84.2	76.4	76.2	57.8	57.4	52	51	34.8	30
150mins		68.6	89.2	80	79	60.2	60	55.2	55	37.6	32.2

DISCUSSION

The solubility result obtained shows that the wax precipitate got dissolved in the solvents as the contact time increases. From table 4.4, it can be seen that 100% Toluene dissolves the wax precipitate within the shortest contact time while 100% Kerosene dissolves it within the longest. From figure 4.1 which shows the plot of percentage solubility against time for the various solvents: 100% toluene, 100% kerosene, 90:10, 80:20, 70:30, 60:40,50:50, 40:60, 30:70, 20:80,10:90 toluene: kerosene solvent mix. The curve of 100% toluene shows maximum increase in solubility as contact time increases and thus its contact time could not go beyond 70mins. This shows that the remediation of wax using toluene will be very effective and will reduce shut in period but it is a very expensive method and it has been a challenge to the oil industry especially in places with problems of wax deposition.

For 100% kerosene, the result is not as effective as that of 100% toluene, it finally dissolved the wax but it took a longer contact time of 150mins. From fig4.1, the curve of kerosene stretched over a longer period of time which means its solubility increases with increase in contact time. Kerosene is a very cheap method of wax remediation and is readily available but it will in turn increase the downtime. The 70:30 toluene: kerosene mixture dissolves the wax completely within a total contact time of 120 mins, this will be a less costly operation but because of its longer contact time it is not advisable because it will cause delay in operation. The 90:10 and 80:20 toluene: kerosene mixture shows similar response to their contact time and completely dissolves the wax precipitate within a total contact time of 90mins which is almost similar to the performance of 100% toluene which completely dissolves the wax precipitate within the contact time of 70mins. Thus, both the 90:10 and 80:20 toluene: kerosene solvent mixtures can lead to an effective wax remediation operation. But in the case whereby cost of great importance, the 80:20 toluene: kerosene mixture will be highly recommended because it is cheaper.

From figure 4.2, 100% toluene still shows maximum increase in solubility as contact time increases and thus its contact time could not go beyond 70mins.For 100% diesel, the result is not effective as that of 100% toluene; in fact compared to 100% toluene, the solubility result is quite poor. From figure 4.2, the curves for the 90:10, 80:20, 70:30,60:40, 50:50, 40:60, 30:70, 20:80, 10:90 toluene: diesel mixture all stretch over a longer period of time which means that they could not achieve 100% solubility within the total contact time and thus, will require longer period of time to dissolve the wax completely. Thus, the use of diesel will not lead to an effective wax remediation operation because it will require a lot more time to completely dissolve the wax and this can in turn increase the downtime hence, increases cost.
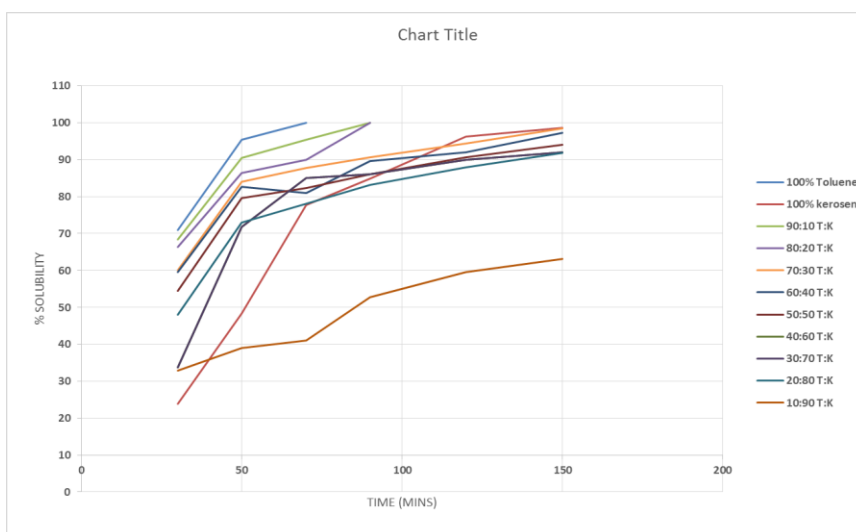
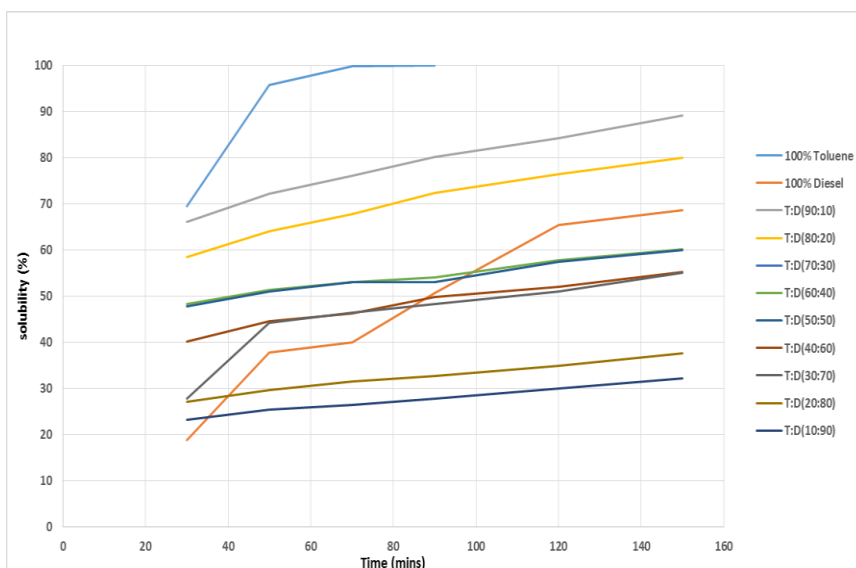**Figure 5: Plot of Solubility (%) against Time for Toluene: Kerosene Solvent mix**

Figure 6: Plot of Solubility (%) against Time for Toluene: Diesel Solvent mix

CONCLUSION

The aim of this research project is to demonstrate the solubility of wax precipitate using different solvents with time variation. From the results obtained, it is possible to select an appropriate solvent or solvent mixture for cleaning wax deposited in production tubing and even crude oil pipelines. The results showed that using 100% kerosene and 100% diesel is not an advisable option because it took 150 mins for the former to dissolve the wax completely and the latter could not achieve 100% solubility within the total contact time of 150mins. The use of 100% toluene presents a better but rather expensive option since it dissolved the precipitated wax over a comparative short period of 70mins. The 90:10 and 80:20 toluene: kerosene mixture shows similar response to their contact time in that they both dissolved the wax completely in total time of 90 mins which is almost similar to the 70mins in which 100% toluene achieved complete solubility. Thus, both 90:10 and 80:20 toluene: kerosene mixture can be recommended for effectively cleaning wax deposits but since the 80% toluene and 20% kerosene mixture is less expensive, it is therefore highly recommended for an effective wax remediation operation.

This research can be used to as a guideline in selecting a less expensive chemical method of wax remediation. The 80:20 toluene: kerosene mixture can be produced in large quantities to clean wax deposits in crude oil tubing and pipelines, it assures a reduced contact time with effective output as well as a cost effective operation. Subsequently, in a situation whereby time is not an issue and cost is of great importance, other solvents such as 100% kerosene, 100% diesel and the different mixtures of toluene-kerosene and toluene- diesel mixtures can also be used.

REFERENCES

Addison, G.E. (1984). Paraffin Control more Cost Effective. SPE 13391. Eastern Regional Meeting, Charleston, WV Oct. 31- Nov. 4, 1984.

Furniss B.S (1989). Vogel's Textbook of Practical Organic Chemistry, 5th edition, Longman/ Wiley, New York.

Brown, W. Y. (1640). Prevention and Removal of Paraffin Accumulations. Drill. and Prod. Pract., API 1940, pp. 85-96.

Bucaram, S. M. (1967). An Improved Paraffin Inhibitor. J. Pet. Tech., Feb 1967, pp. 150-156.

Burger, E. D.; Perkins, T. K; Striegler, J.H.J. (1981). Petroleum Technology 3, pg. 1075-1086.

Ceresana (1990). Toluene- Study: Market, Analysis, Trends.

Gruse, W.A. and Stevens, D.R. (1960). "Chemical Technology of Petroleum. McGraw-Hill", New York. Chapter 12.

Mills, R. Van A. (1923).The Paraffin Problem m Oil Wells. BuMines RI, Serial No. 2550, Dec, 1923, 11 pp.

Newberry, M. E (1984). Chemical Effects on Crude Oil Pipeline Pressure Problems, J. Pet. Tech., pp. 779-786.

Reistle, C.E.: (1932). Paraffin and Congealing Oil Problems," Bull. USBM, No. 348

Reistle, Jr., C. E. and O. C. Blade. (1932). Paraffin and Congealing-Oil Problems. BuMines Bulletin 348, 1932,.171 pp.

Sadeghazad, A.; Chrisriansen, R.L.; Sobhi, G.A.: (1998). Wax Precipitation Factors and Deposition Mechanisms, Third National Chemical Eng. Congress, Ahwaz-IRAN, 1998.

Speight, J.G. (1999). "The Chemistry and Technology of Petroleum". 3rd Edition. Marcel Dekker, New York.

Weingarten, K. J., Rodwel, M. J. W., & Bloom, D. M. (1988). Picosecond optical sampling of GaAs integrated circuits. IEEE Journal of Quantum electronics, 24(2), 198-220.

Wright, J. C. (1951). Paraffin Prevention and Removal in Wells in South eastern Ohio. Drill. and Prod. Pract., API 1951, pp 380-388.