

DEPOSITION OF PARAFFIN WAX  
FROM FLOWING SYSTEMS

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August 1977

## ABSTRACT

Factors affecting the deposition of paraffin wax from its solutions with hydrocarbons onto surfaces in pipelines and process equipment are discussed.

Deposition studies showed that paraffin deposition increases asymptotically with time to reach a final fluctuating value. The deposition decreased with flowrate and bulk temperature but increased with concentration. The asymptotic deposition was inversely proportional to the flowrate squared.

It is suggested that paraffin deposition is controlled by the cohesive properties of the wax. For the conditions studied, there appears to be a critical deposit thickness at which deposits break up and slough away giving rise to the fluctuating condition.

## 1. INTRODUCTION

The problem of paraffin wax deposition from waxy feedstocks is of long standing in the oil processing industry and continues to attract research and discussion<sup>(1)</sup>. It is of particular importance in the transportation of oil through pipelines with major difficulties arising during restarting after shut down and in subsequent processing in equipment such as heat exchangers<sup>(2)</sup>. Information and data which help to provide a better understanding of the problem is therefore of interest to designers and operators of process plant.

## 2. PROPERTIES OF WAXY HYDROCARBONS

In the oil industry paraffin deposition is referred to as the formation of any predominantly organic matter in oilwell tubing, surface flowlines and other production equipment<sup>(3,4)</sup>. The deposits consist mainly of n-paraffins with smaller amounts of branched and cyclic paraffins and aromatics<sup>(5)</sup>.

Of prime importance is an appreciation of the temperature at which wax crystals appear in a solution, and the temperature at which movement is arrested for a specific time. The standard empirical tests, the 'cloud point'<sup>(6)</sup> and the 'pour point'<sup>(7)</sup> respectively have been devised to give such information. The solubility of wax in the oil with respect to temperature is clearly related to these tests and empirical relationships have been published from which solubilities may be calculated<sup>(8,9,10,11)</sup>.

The property which may be termed 'viscosity' is difficult to define in relation to wax laden hydrocarbons. The rheological property is a function of temperature and the magnitude and rate of shear applied to the solution<sup>(12,13,14,15,16,17)</sup>. In addition the rheological properties will be affected by the state of the solution, ie whether or not it is flowing or stationary.

The crystalline nature of paraffin wax has been investigated by a number of workers<sup>(18,19,20)</sup>, and the modification of the wax crystals by additives during deposition or gelling can improve the flow properties<sup>(21,22)</sup>. Heat treatment has also been found beneficial in the improvement of pumping of certain waxy crude oils.

## 3. DEPOSITION ON SURFACES DURING HEAT REMOVAL

Papers have been published which give data on the effects of heat loss from

pipelines carrying waxy oils<sup>(23,24)</sup>. In some respects these effects are related to cooling which could occur in processing equipment notably oil coolers. The lower temperatures produced can give rise to crystal formation if the temperature of the oil is reduced below the cloud point for the particular solution under consideration. Even under conditions where the bulk flowing oil is at a temperature above the cloud point temperature, the oil near the confining wall may well be at a temperature which is below the critical cloud point temperature. The physical picture will depend very much on the flow conditions and temperature distribution.

### 3.1 Flowrate and Time

Jessen and Howell<sup>(25)</sup> studied the effect of flowrate on paraffin wax deposition in steel and plastic coated steel pipes. Their apparatus consisted of 2 cm pipe 150 cm long submerged in a cold water bath. From a 135 litre reservoir in a hot water bath, microcrystalline wax in kerosene solutions and several crude oils were circulated for about 3 hours. In all the runs the solution bulk temperature was kept below its cloud point.

The main conclusion of the work was that in laminar flow, the estimated deposition increased with flowrate, reaching a maximum prior to transition to turbulent flow and then decreasing with increasing turbulence. The increase in deposition, in laminar flow, with increased flowrate, was explained in terms of more particles being carried by the moving stream, providing a greater opportunity for deposition on the pipe surface. Furthermore, viscous drag exerted by the stream tends to remove the accumulation and, at high velocities, becomes equal to or may exceed the shear stresses within the deposited wax, thereby providing a removal mechanism. Paraffin deposited at high flowrates was observed to be considerably harder than paraffin deposited at lower flowrates. The increase in both viscous drag and shearing stresses in the paraffin deposit at high flowrates was considered to account for the gradual decrease in deposition at high flowrates.

Tronov<sup>(26)</sup> studied the effect of flowrate on paraffin deposition using a 5 per cent solution of technical paraffin in kerosene. The apparatus used consisted of a room temperature reservoir from which the solution flowed to an experimental chamber. The paraffin deposited on the outside of a jacketed tube cooled from the inside with water 10°C below ambient. Neither the melting point of the wax used nor the solution cloud point were given. The thickness of the paraffin deposit was measured after 2 minutes by a camera fitted with a microscope.

The results obtained show that the deposit thickness decreases with increasing velocity and that the deposit hardness, as expressed by the velocity required to remove it from the tube wall, increases with velocity. The behaviour was explained by concluding that as the flowrate increases only those wax crystals and crystal clusters capable of firm attachment to the surface, and having good cohesion with one and other, will not be removed from the deposit.

The conclusion is supported by Eaton and Weeter<sup>(27)</sup> using a rotating disc apparatus; the rate of deposition was shown to be low at extreme velocities and much higher at intermediate values.

The studies on paraffin deposition indicate that the build-up of deposits alternates with their partial or total removal, independent of the nature of the surface. For example, it has been observed that deposits are removed from a glass surface in large lumps leaving the surface very clean.

Armenski et al<sup>(28)</sup> in a paper analysing reduction in pipe diameter due to paraffin deposition, observed slight removal of deposits following their establishment. During the cooling of waxy kerosene in simulated heat exchanger tubes, fluctuating deposit thickness has been observed<sup>(2,29)</sup>.

Patton and Casad<sup>(30)</sup> studied paraffin deposition on a cold surface inserted into a well stirred wax solution maintained above its cloud point temperature. They found that deposition increased asymptotically with time. The initial rate of deposition and the asymptotic deposit both decreased with increased stirring. Hunt<sup>(3)</sup> and Patton and Jessen<sup>(4)</sup> found that paraffin deposition increased asymptotically with time.

### 3.2 Crystallisation and Temperature

The size and number of the crystals formed in solution is important in any deposition process, and then in turn is dependent upon the rate of cooling. Tronov<sup>(26)</sup> stated that a high rate of cooling favoured the formation of a large number of small crystals. Rafikov et al<sup>(12)</sup> studying paraffin based petroleum, observed that on rapid cooling many centres of crystallisation arise, which lead to the formation of fine crystals. On slow cooling Rafikov et al observed that the crystallisation process occurs under more uniform conditions, as a result of which large, more uniformly packed crystals are formed, which possess a relatively small specific surface area and free energy. Paraffin crystals formed under slow cooling were observed to have less tendency to form solvated

systems and strong structural networks, than crystals formed under rapid cooling.

Closely related to the rate of cooling is the temperature difference between the bulk solution and the cold surface. Eaton and Weeter<sup>(27)</sup> found, as might be anticipated, that the rate of deposition of wax increases steadily with the increase in temperature difference.

Cole and Jessen<sup>(31)</sup> studied how the temperature difference between a solution cloud point and a confining surface, affected paraffin deposition by passing a kerosene-wax solution at a low flowrate over a chilled copper plate for 2 hours. The solution used throughout the work contained 8 per cent of a 63°C melting point refined paraffin with a cloud point of 33°C. The temperature of the solution was maintained at 38-39°C, so the paraffin would remain in solution and the plate temperature varied from 4 to 32°C. The amount of paraffin deposited was determined by removing the copper plate and weighing it. The temperature difference between the cloud point and the plate temperature was considered most important in controlling the accumulation. It was found that the paraffin deposit contained 8 per cent kerosene. The paraffin was in crystalline form, but the retained kerosene was enough to make its consistency that of a heavy paste. The experimental results showed that deposition increased with increasing temperature differential.

Patton and Casad<sup>(30)</sup> stated that the amount of paraffin deposited on a surface will increase as the temperature differential between the surface and the solution is increased. The deposition will only occur if the surface temperature is below both the temperature of the solution and the solution cloud point.

Further experiments by Cole and Jessen<sup>(31)</sup> showed that the initial rate of deposition increased with increasing temperature differential. The change in rate of paraffin deposition was attributed to the thermal insulation by the deposited wax layer and the variation in the amount of paraffin available for deposition, per degree temperature differential, since the rate of change in paraffin solubility with temperature is much greater just below the cloud point than it is for lower temperatures.

Apart from the effect on crystal growth temperature difference will affect composition since the wax in solution is a mixture of compounds and will separate out according to melting point distribution. As the temperature

difference between the tube wall and the oil increases the deposits become looser since on rapid cooling both high and low melting point paraffins will crystallise simultaneously forming a weak porous structure with cavities full of oil. Finally, the rapid fall in the quantity and melting point, as the oil temperature decreases, confirms that the mechanism of paraffin deposition is one of crystal growth directly on a surface.

### 3.3 Surface Properties

Since deposition and particularly the adhesion of the deposit onto a surface will be a function of the surface properties investigations into the effects of different surfaces have been carried out.

Parks<sup>(32)</sup> demonstrated that the presence of certain adsorbed films on a metal surface would reduce the adherence of paraffin to that surface. Zismann<sup>(33)</sup> showed that the nature of the compounds adsorbed on a surface would determine its wettability characteristics.

Cole and Jessen<sup>(31)</sup> studied the effect of wettability on paraffin deposition and found that the amount of wax deposited for a given temperature difference decreased with decreasing free surface energy. It was found that the temperature difference and free surface energy acted independently in determining the amount of wax depositing. Cole and Jessen concluded that as paraffin wax is deposited on a surface it is held in place by adsorption forces. These adsorption forces are dependent upon the free surface energy possessed by both the paraffin and the surface. As the free surface energy of the plate is reduced, a resultant decrease in the adsorption forces holding the paraffin to the plate surface takes place. This causes a decrease in the amount of paraffin which can be retained on the plate surface for the flow conditions present. Patton and Jessen<sup>(4)</sup> investigated the effect of wettability on paraffin deposition. They found that deposition increased with increased free surface energy of the deposition surface.

Hunt<sup>(3)</sup> studied the effect of roughness of paraffin deposition and concluded that deposits do not adhere to metals themselves but are held in place by surface roughness. Jorda<sup>(5)</sup> investigated the roughness effect in deposition. Paraffin deposition was found to increase with surface roughness. Patton and Casad<sup>(30)</sup> performed similar studies and concluded that no correlation could be observed between surface roughness and deposition. However, they argued that the adhesion bond at a surface should be proportional to the total contact area and therefore related to surface roughness.

### 3.4 Deposition Factors Summarised

The deposition of wax from hydrocarbon solution appears to be characterised by an asymptotic approach to a final value influenced by three main factors; flowrate, temperature distribution and chemical nature.

1. Increased flowrate decreases wax deposition and increases the strength of deposits.
2. Deposition increases with increased temperature difference between the solution cloud point and the wall temperature. The rate of deposition gradually decreases due to the thermal insulation of deposited wax, until a final asymptotic value is reached. If a solution contains a range of waxes, the strength of deposits will decrease with increased temperature differential.
3. Chemical nature of the wax and the solution can affect the deposition process by modifying the adsorption forces holding deposits in place. The structure of wax crystals, depending as it does upon the chemical composition and rate of production, will also be important. The structure of the resulting layer in any deposition process generally is unlikely to be uniform because of these and other factors, allowing planes of weakness to develop which in turn give rise to a random process of growth and removal of the wax layer.

### 4. DEPOSITION AND REMOVAL MECHANISMS

The mechanisms of growth and removal of wax deposits are likely to be extremely complex, bearing in mind the foregoing discussion. Of paramount importance however, is the temperature distribution between the bulk of the flowing fluid and the cold wall on which the deposition takes place.

Assuming that the bulk temperature is above the cloud point of the solution and the wall temperature below this critical temperature, it will be possible for wax particles to be formed in flowing systems. In turbulent flow, location of crystal formation may either be in the turbulent core or in the laminar boundary layer depending upon the temperature distribution conditions. In general it is likely that particles will appear in the laminar boundary layer since the largest temperature change will take place across this layer.

Experimental results have been obtained for a flowing system where paraffin wax-kerosene solutions were cooled in tubular heat exchangers<sup>(2)</sup>. It was found that the overall heat transfer resistance increased rapidly to some average

value that fluctuated at random with time. These fluctuations were apparently caused by continuous build-up and break-down processes of the wax deposit. The creation of planes of weakness and the increase in shear stress at the wall as deposits build up were probably the main factors causing break-down and removal.

The experimental work showed that the average wax deposition decreased with flowrate. Heat, mass and momentum transfer all increase with flowrate. While heat and mass transfer are necessary for deposition to occur, the deposition at asymptotic conditions is probably more dependent on momentum transfer in the form of shear stresses at the wall. The transport of material to the surface is therefore not the limiting factor, but the cohesive properties of the particles depositing. Increased temperature and concentration will decrease and increase the number of particles available for deposition, respectively, and also affect their cohesive properties.

## 5. EXPERIMENTAL

A deposition assembly was designed and constructed to simulate deposition of paraffin wax in heat exchangers. The flow diagram of the apparatus is shown in Figure 1. Essentially the equipment consisted of two closed circulation loops where paraffin wax from wax/kerosene mixtures was allowed to deposit on a copper plate cooled by water. The experimental solution and the cooling water were circulated through rectangular ducts separated by the deposition plate. A long entry section to the duct was provided to ensure that the velocity profile in the experimental section had been fully developed before the plate was reached by the fluid. A diagram of the duct assembly is shown in Figure 2. The pipework in the circulation system was steam traced to eliminate unwanted deposition. The solution and cooling water inlet and outlet temperatures were measured with mercury-in-glass thermometers. Temperatures were maintained constant by the appropriate control of immersion heaters. Flowrates were measured by calibrated orifice meters.

The bulk temperature of the paraffin wax-kerosene solution was kept  $5^{\circ}\text{C}$  above its cloud point temperature. The solution flowrate in all runs was  $0.116\text{ kg/s}$  such that the Reynolds number was greater than 5000 and the flow conditions therefore turbulent. The cooling water flowrate was  $0.127\text{ kg/s}$  and its bulk temperature  $15^{\circ}\text{C}$  in all the experimental runs. The temperature drop of the experimental solution and the cooling water across the deposition assembly was negligible.

The amount of paraffin wax depositing was estimated after a measured time by removing the copper plate and weighing it before and after cleaning. The experimental results show the deposition with time. No deposition was observed on the water side of the deposition plate.

The copper plate was sand-blasted to be more like a commercial surface than a smooth polished surface. The blasting medium was described as 30/40 mesh.

Experimental solutions with two different waxes were used; 51/54°C and 57/60°C melting point fully refined paraffin wax in kerosene. The 51/54°C solutions were 8.5, 10.0 and 11.5 per cent by weight with the cloud point temperatures 18, 20 and 22°C respectively. The 57/60°C solutions were 2.5 and 3.5 per cent by weight with the cloud point temperatures 20 and 23°C.

Figure 3 shows a typical plot of deposition with time for 2.5 per cent 57/60°C wax with cloud point 20°C and solution bulk temperature of 25°C. Figure 4 shows the effect of flowrate for 3.5 per cent 57/60°C wax with cloud point temperature 23°C and bulk temperature 28°C. The deposition was determined after 15 minutes. Figure 5 shows the effect of concentration for 8.5, 10.0 and 11.5 per cent 51/54°C paraffin wax in kerosene.

## 6. DISCUSSION AND CONCLUSIONS

The experimental results demonstrated the asymptotic nature of paraffin wax deposition. The amount of paraffin wax depositing increased with time to reach a final fluctuating value. The terminal value of deposit weight was obtained in a shorter time at higher concentrations. As expected, the deposition decreased with increased flowrate.

The wax deposit were found to cover the deposition plate evenly and the layer was firm in nature although the degree of firmness decreased with concentration. At experimental times approaching two hours the deposits appeared to wear away at the leading edge of the deposition plate. Good adhesion to the plate was apparent since it was not easy to remove the wax film from the plate. The results suggest that the paraffin deposits broke down earlier at higher concentrations; it is considered that break-down would occur when a certain critical thickness was reached.

It is apparent from the literature and the present studies that deposition

(initial and asymptotic) decreases with flowrate and increases with concentration and the temperature difference between the cold wall and the solution cloud point<sup>(2,5,12,26,30,31,34)</sup>. In most practical situations it is probably difficult to alter the temperature conditions and the solution concentration. However, in some circumstances the solution flowrate may be adjusted to affect the paraffin wax deposition process. Since paraffin deposition grows rapidly to an asymptotic thickness, designers and operators of pipelines and heat transfer equipment are interested in the average amount of deposition at asymptotic conditions. It is therefore of interest to know how the asymptotic deposition depends of flowrate.

The experimental data of Bott and Gudmundsson<sup>(2)</sup> gives the asymptotic deposition (as fouling resistance) at various flowrates (as Reynolds number) and is shown in Table 1. The asymptotic fouling resistance was plotted against the inverse

TABLE 1  
Experimental Fouling Resistance at Asymptotic Conditions<sup>(2)</sup>

Run	Reynolds Number	Bulk Temp (°C)	Fouling Resistance (kW/m <sup>2</sup> °C) <sup>-1</sup>
B1-5	7635	42.5	2.1864
B6-9	13311	42.8	1.5359
B10-13	6716	42.4	3.0117
C1-14	8890	38.2	2.2584
C5-16	6888	38.2	3.2116
C8-20	4635	38.1	5.6461

Note: Wax concentration 26% weight  
Solution cloud point 32°C  
Cold wall temperature ~ 7°C

of the Reynolds number squared in Figure 6 and found to fall on a straight line. Therefore, the asymptotic deposition is inversely proportional to the flowrate (Reynolds number) squared.

ACKNOWLEDGEMENTS

The authors would like to thank the Science Research Council and the Heat Transfer and Fluid Flow Service for the provision of funds to enable the work reported to be carried out.

NOTE ON FIGURES

All the Figures in this paper are presented elsewhere in Part II of the Thesis. These are therefore not repeated here but, instead, the appropriate Thesis Figure numbers given in the following table:

Paper	Thesis
Fig 1	Fig 10
Fig 2	Fig 11
Fig 3	Fig 15
Fig 4	Fig 17
Fig 5	Fig 18
Fig 6	Fig 19

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