Paraffin Wax Deposits and Chemical Inhibitors

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INTRODUCTION

The accumulation of paraffin wax in petroleum reservoirs and production equipment remains a continuous problem and expense in the production of oil. These problems have been remedied in the past by scrapers, hot-oil treatments and solvents. However, with the advent of extremely deep production, offshore drilling, and the possibility of ocean floor completion, the application of remedial measures becomes economically prohibitive. As a result, the use of chemical additives as paraffin deposition inhibitors has become necessary.

Since no one additive has been proven universally effective, the problem of selecting an efficient additive for a specific application is presented. In order to define a suitable additive, a better understanding of the mechanisms of inhibition is necessary.

Previous work showed that high molecular weight fractions from crude oil significantly affected paraffin crystal growth and subsequently retarded or prevented paraffin deposition.[1,2] Some investigators found that these fractions were preferentially adsorbed to a metal surface and that a reduction in deposition occurred.[3,4] In addition, it was noted that decreased deposition could be attributed to modifying the paraffin wax crystals or changing the wetting characteristics of the pipe surface.[5-13] Although there is considerable experimental evidence to support each mechanism, there is no way to predict which mechanism and chemical inhibitor is the most efficient way to prevent wax deposition for any given crude oil system.

PARAFFIN WAX ACCUMULATION

The areas of paraffin control and/or prevention are complicated by what appear to be several different theories regarding the mechanism of paraffin wax accumulation and inhibition. Generally, most investigators agree that the direct growth of paraffin wax crystals causes the more severe deposition. A micro-moving picture used to record paraffin deposition in a flowing well revealed that nucleation of paraffin crystals occurred directly on the metal surface.[14] The paraffin crystals already in suspension usually were deposited in quiescent parts of the equipment. Gas bubbles were found not to act as nucleation points for paraffin crystals; however, the evolution of gas did decrease the solubility of paraffin in oil.

Hunt and Jorda stated that surface roughness was the only factor controlling the amount and characteristics of paraffin deposits.[15,16] However, the use of plastic tubing of tetrafluorethylene, polyethylene or polypropylene, which were extremely smooth, still resulted in "massive" deposits. This phenomenon was attributed to a high chemical attraction between paraffin wax and the plastic pipe by hydrogen bonding or some form of co-crystallization.

Nye found a good correlation to exist between the pour point of a crude oil and the degree of paraffin deposition experienced in the field.[17] There was also a good correlation between the degree of paraffin deposition, the total amount of saturated hydrocarbons present in a crude oil, and the cloud point temperature of the saturated hydrocarbon fraction. Jessen postulated that the deposition of paraffin was not directly related to the low pour point but to another mechanism, possibly involving the adsorption of specific compounds to the pipe wall, which led to a greater degree of paraffin deposition than expected.[17] Accordingly, it was concluded that no matter what the mechanism, it was more significant than the pour point correlation. In support, Patton found that the presence of an adsorbed crude film on a steel surface increased the surface energy of the metal and caused greater deposition.[1]

Jessen also pointed out that extremely high water production often prevented paraffin deposition where it would normally have been expected.[17] However, some wells with extremely high water production also experienced severe paraffin problems. A possible explanation for these two conflicting results was given by Shock and Kimbler.[18,19] Shock attributed the decrease in paraffin deposition accompanying an increase in water production to the greater specific heat of water which maintained a higher temperature in such wells in comparison with those producing only oil. In contrast, Kimbler found well-oriented monomolecular films at crude oil-water interfaces and proposed that these films result in water-wet pipe surfaces which provide a place for microscopic crystal growth of wax, which in turn could produce "massive" deposits.

In addition, the association of asphaltenes and paraffin wax in wax deposits has been mentioned by several investigators.[18,20,21] It is interesting to note, also, that Preckshot found that bitumen deposits possibly were associated with an electro-depositional effect.[22] He found that asphaltic material had a negative charge and could be deposited electrolytically. Preckshot reasoned that a flowing stream of oil could produce a streaming potential which would cause the colloidal asphaltic material to deposit on the pipe. Along the same line, Gutsalyuk and Yatsenko found that paraffin wax acted as a selective adsorbent for the tar in cracked residue.[23] Hanke also believed there existed a strong association between asphaltenes and high molecular weight paraffin wax which could result in a gel formation and secondary accumulation of paraffin.[3] Greenlee concluded that an insufficient concentration of resins and aromatics in crude oil prevented effective suspension of colloidal asphaltenes which caused a paraffin deposit.[24]

INHIBITION OF PARAFFIN DEPOSITION

Early investigators recognized that asphaltenes, aromatics, and resins play an important role in the crystal habit of paraffin waxes. In some studies dealing with dewaxing of oil, resins and aromatics were found to be the cementing materials in wax clusters, and asphaltic material acted as the crystallizing agent for better filtration rates.[25] Later, several people attributed crystal habits to different homologous series of hydrocarbons that could crystallize as either needles, plates, or small malformed crystals.[26, 27] Other investigators were of the opinion that needle crystals were small plates turned on edge.[4,2]

This idea of differently shaped crystals and how they affected filtration rates in the dewaxing process and pour points for fuel oil, generated increased interest in the paraffin deposition work. Howell found that small amounts of asphaltenes lowered the pour point of kerosene wax solutions considerably and reduced paraffin deposition.[28] Others showed that long-chain alkyl polymers were effective in depressing the high pour point oils while the shorter alkyl polymers were effective on low pour point oils.[29]

Lorenson concluded that alkylated aromatic-type dispersants and methacrylates were either adsorbed, or co-crystallized on the surfaces of crystallized wax, which promoted growth in new directions.[30] The irregular growth prevented any crystal network from being established in oils and reduced the pour point. In a like manner, Birdwell and Chichakli observed this change in crystal size and shape and concluded that the same mechanisms of crystal modification which were responsible for pour point depression were also causing a reduction in paraffin deposition.[4,2] That is, although the modified crystals could become attached to the pipe wall, the restricted growth prevented agglomeration, and the viscous drag from the flowing oil prevented substantial accumulation.

Polycyclic aromatics were found to be good paraffin inhibitors when added in the presence of asphalt.[31] It was postulated that the molecule "acted by attaching itself to or solvating the colloidal asphalt particle", thus preventing nucleation on the colloid. The resulting paraffin crystals were small and easily dispersed.

Several investigators have used polyethylene as a crystal modifier and found it to be effective when other polar substances or dispersants were present. Briant concluded that polyethylene created a network inside which the paraffin molecules could settle, forming numerous tiny crystals.[32] Similarly, Mieulet and Pernado believed that the inhibiting mechanism was the formation of a network to which paraffin microcrystals became attached providing a scattering effect during crystal growth and agglomeration which was a function of polyethylene concentration, structure, and molecular weight.[33]

Bucaram, on the other hand, thought that inhibition with polyethylene depended on a similarity between the structures of the paraffin molecules and the polymer molecule.[34] This similarity allowed the polyethylene molecule to incorporate into the growing wax molecule and prevent additional growth by virtue of the branched structure of the polymer.

Additional mechanisms of inhibition relate to preferentially adsorbed films on the pipe surface which either repel wax crystals or prevent strong bonding between the metal and the paraffin wax. Whether the mechanism is one of dispersion or an adsorbed film which lowers the surface energy of the metal, is questionable. Hasiba and Hanke found that preadsorbed films of heavy crude oil fractions on a metal surface would reduce the surface energy of the metal and prevent strong bonding by the wax crystal.[35,3] Hasiba believed that there must be enough polar material in solution to establish an equilibrium between desorbed and adsorbed film material. Patton found that paraffin deposition was enhanced by an adsorbed film unless polar material was added to the wax solution.[1]

PARAFFIN SOLVENTS AND INHIBITORS

Commercial chemicals available for treating paraffin wax problems are discussed below under four basic headings. These four groups are solvents, wetting agents, dispersants and crystal modifiers. For any given chemical inhibitor, one or several of these agents may be combined to provide the desired inhibitive characteristics for efficient treating.

Solvents generally are used for remedial treatment of paraffin deposits and for minor wax problems. Some of the best solvents, such as the chlorinated hydrocarbons and carbon disulfide, have restricted use because of the detrimental effect on refinery catalysts and health hazard problems. Other solvents such as refined aromatics, aliphatics, butanes and pentanes have had some success in treating minor paraffin problems. In theory the solvents reduce the cloud point of the crude oil below the producing temperature which prevents the formation of paraffin crystals. In most cases, however, the quantity of solvent necessary to produce this effect is prohibitive and uneconomical. Generally these solvents are used for slug treatment of plugged flow lines and tubing or as the carrying agent for some of the other inhibitors.

Wetting agents and dispersants comprise the majority of chemicals used as paraffin wax inhibitors. These chemicals are closely related as to their mechanism of inhibition and chemical composition, the general difference being that a dispersant is an oil-soluble compound and the wetting agent is a water-soluble compound. For example, ethoxylated phenols may have from 1 to 20 ethylene oxide groups attached to a phenol. The phenol end of the molecule is oil soluble and the ethoxylated group is water soluble. As the number of attached ethoxylated groups are increased from 1 to 20, the compound becomes more water soluble. In the 1-4 range, the ethoxylated phenol is oil soluble. From 5-9, the compound may be oil soluble or water soluble depending on the water salinity. This group of compounds are very good emulsifiers since the surface tension between the oil and water phase is reduced to almost zero. In the 10-20 range, the compound is water soluble because the large number of ethoxylated groups drag the compound into the water phase.

Dispersants, in theory, coat paraffin crystals as they crystallize with oil. The adsorbed film retards growth and repels similarly coated crystals and metal surfaces. The small crystals remain suspended in the oil phase which prevents wax accumulation.

In a similar way, the emulsifying compounds are used to suspend paraffin crude in a water phase during production to reduce wax deposition.[36] Successful results seem to require a minimum water-cut of 35 per cent.

The wetting agents water-wet the metal surfaces which prevents strong adhesion by wax crystals. Theoretically, substantial accumulation is restricted by the weak bonding to the pipe surface and the shearing forces created by the producing fluid.

Crystal modifiers are relatively new and may provide the most efficient means of reducing or preventing paraffin wax deposition. They may consist of polyethylenes, methacrylates, or any branched-chain polymer which will cause deformed or modified crystal growth. Their mechanisms of inhibition may be any one of three as outlined by Bilderback.[37] Some modifiers cause nucleation above the cloud point of the crude oil and the wax molecule is extended and discrete. At the cloud point, the modifier co-crystallizes with the paraffin wax. Below the cloud point the modifier adsorbs to the wax crystals. All three mechanisms restrict normal crystal growth which, in turn, lowers the cohesive forces between the wax crystals and prevents the formation of a strong intercrystalline network. As a result, the wax crystals which do adhere to a surface are weakly held and provide no stable means of growth for additional crystals.

In addition to the commercial chemical inhibitors, there are several naturally occurring compounds in crude oils which are very good paraffin wax inhibitors. The aromatics are excellent paraffin solvents, while the resins and asphaltenes have both been identified as good crystal modifiers and dispersants.

These compounds alone may represent a more important factor in paraffin wax problems during production, than the percentage of paraffin wax in the oil. In some cases, a slight loss of aromatics during production could reduce the asphaltene solubility and, therefore, change the natural inhibitive characteristics previously available. A small addition of an aromatic may reestablish the original aromatic-asphaltene balance and provide complete paraffin control; in other cases, it may be an imbalance of several compounds which could be provided by treating with another crude oil. In any case, natural inhibitors could provide an inexpensive paraffin control chemical. The problem remains, however, as to how one can effectively evaluate any given crude oil system, and prescribe the necessary treatment without going to the expensive and sometimes endless method of trial and error.

EFFECTIVE EVALUATION OF CHEMICAL PARAFFIN INHIBITORS

Proper treatment recommendations for preventing or decreasing paraffin wax deposition at the least cost are complicated by the individuality of the crude oil produced and the wide selection of chemicals available for treating this problem. In addition, several postulated mechanisms of deposition and inhibition affect the proper selection of treating chemicals. As a result, the combined variables propose such a complex system that prescribing proper treatment also becomes as equally complex.

There are several tests used by chemical companies for evaluation and recommendation of treatment with their products. Usually these are static tests confined to only those products marketed by the testing company. The fact that the tests are static and the number of chemicals examined are limited gives neither a comparison to other available chemicals nor an understanding of how the tested chemicals affect the crude oil in question.

The testing of every available chemical is impractical; however, in some recent laboratory research, four separate tests were used to evaluate several chemicals as inhibitors of paraffin wax deposits.[38] The results not only provided a good evaluation of an additive's effectiveness, but also indicated how and why a particular additive did or did not work. More importantly though, the results may lead to alternative additives which would provide the proper mechanisms for effective inhibition. In addition, there are several inhibitors that have proven effective in different areas, but they may be made to work better if it were known how they worked and what was lacking.

The four tests used consisted of:

1. An apparatus to study the flow characteristics of crude oil at temperatures below the cloud point, and the effect of various additives on these cold flow properties;
2. An apparatus to deposit paraffin wax from crude oil under dynamic conditions;
3. A chromatographic column to separate the saturate fraction from the deposited paraffin wax; and
4. A system for studying the molecular weight distribution in the saturate fraction of the paraffin wax deposit.

The chemicals tested were known dispersants, film wetting agents and crystal modifiers as defined by previous research. Detailed descriptions of these tests and additives used may be found in a publication by the Texas Petroleum Research Committee (see Ref. 38).

The results were important only as a way to reach a better understanding of the mechanisms of inhibition rather than the success or failure of the individual chemicals tested. The tests revealed that both crystal modification and dispersion were effective mechanisms for decreasing paraffin wax deposition. Asphaltic additives, which were labeled as film wetting agents, also reduced deposition in some isolated instances.

Even more significant was the fact that the additives were found to be selective in regard to the molecular weight of the wax crystals inhibited. The average molecular weight of the paraffin wax deposits increased substantially with improved inhibition. Those additives which were not effective as inhibitors, produced little or no change in the composition of the wax deposit. This effect was more apparent with the dispersants and crystal modifier than with the film wetting agents.

The concentration of additive used was observed to be extremely important in maximizing the inhibitive effect of the chemical. Correlation between maximum decrease in paraffin wax deposition, maximum increase of cloud point of the saturate fraction from the wax deposit, and maximum decrease of pour point of the crude oil at the optimum concentration of the additive, was extremely good. Increasing the concentration of the additive above the optimum level usually had a detrimental effect on its inhibitive capabilities.

These correlative characteristics suggest possible guidelines to the effective design of an inhibitor treatment when used in conjunction with field tests. Removable test sections in the production equipment would provide paraffin deposit samples for laboratory examination in addition to indicating the relative success of an individual inhibitor being tested. As discussed earlier, these results could be used to suggest other inhibitors that might be applicable.

The use of this procedure requires a good working knowledge of the depositional and inhibitional mechanisms involved, and the inhibitional mechanisms of the chemicals available for treatment. For example, if a crystal modifier or dispersant chemical is effective as an inhibitor for the low-to-medium molecular weight wax crystals, then maybe some film wetting agent could be used to inhibit the high molecular weight waxes. A small amount of solvent may keep the low molecular weight waxes in solution which could reduce the quantity of dispersant needed for proper treatment of the higher molecular weight waxes. There is an endless combination of chemicals that may work, but one must know how and why they work before any intelligent suggestion for treatment can be made.

CONCLUSION

The correlative techniques presented have definite possibilities as guidelines for evaluating and designing the optimum treatment for paraffin wax control or inhibition as long as they are associated with field tests. The correlations are not conclusive or even indicative of an inhibitor's potential success, but indicative of the optimum level of treatment and the mechanism of inhibition. As a result, these tests may show that several inhibitor chemicals from different companies can be blended for the best results. The producer has the advantage of testing any or all chemicals available and designing his own inhibitor treatment as indicated by the tests. The system would eliminate total reliance on a chemical company's recommendation and prevent the waste that is caused by trying one chemical inhibitor after another before the proper one is found.

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