INTELLIGENT TREATEMENT OF WAXY CRUDE OILS

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BACKGROUND

Waxes accumulate as obstructions to the normal flow of crude oil systems. They do this by attracting molecules of like character (e.g., normal paraffin hydrocarbons) and combining through intermolecular forces to form aggregates of a crystalline nature. The aggregates thus formed interact mechanically and accumulate in constricted flow regions, pipe surfaces, and quiescent storage areas. Once it has been determined that paraffin wax accumulation has restricted the normal production, transport, and/or storage of crude oil, measures should be quickly undertaken to remedy the problem. Several remediation methods are available including, hot oiling, hot watering, combination hot water and surfactants, solvent, solvent/surfactant treatments, magnets, bacterial treatments, and crystal modifiers etc… Each method possesses strengths and weaknesses. Hot oiling and hot watering are known to be useful in helping to dislodge pumps that are bound up by wax, but their continued practice has also been shown to concentrate higher melting wax fractions in existing deposits thereby making the remaining deposit more difficult to melt in subsequent treatments. Solvent and solvent/ surfactant treatments are excellent means of wax deposit removal, but the extent of their wax carrying ability is limited by temperatures below the cloud point of wax/solvent combination. Crystal modifiers provide the most effective means of preventing deposits, and will in combination with solvents, or hot oil provide significant deposit removal, but they tend to be costly. The successful treatment of paraffin wax accumulations is largely dependent upon the proper identification and characterization of their chemical composition and their physical behavior under various environmental conditions.

WAX CHARACTERIZATION

Perhaps the best technique for the chemical characterization of waxes in crude oils involves the use of gas chromatography. While this technique has traditionally been limited to hydrocarbons with a maximum carbon chain length of C_{30-40}, high temperature gas chromatography utilizing heat stable columns makes it possible to detect petroleum component waxes up to and including C_{100}. In this way it is possible to identify crude oil paraffin waxes that tend to accumulate and cause problem obstructions in production facilities, pipelines and storage facilities. A high percentage of these obstructions generally consist of linear and branched hydrocarbons with pendant chain lengths of from C_{18} to C_{30+} with a mean distribution centered near C_{24}. Higher carbon number species (e.g., $C_{30-100+}$) are frequently found in some of the heavier or higher viscosity crude oils. Monocyclic and acyclic-branched saturated hydrocarbons tend to dominate this carbon distribution range. Although many of these heavier crude oils contain detectable amounts of C_{60+} hydrocarbons, the viscosity behavior is more characteristic of the higher concentrations of the intermediate carbon chain species. Thus, from the standpoint of pour point and viscosity behavior, it is the much more abundant C_{20-35} fractions that determine the dominant physical characteristics of the oil.

While gas chromatography is an excellent tool, certain physical characteristics of waxy crude oils are best obtained by other means. Pour point, viscosity and deposition tendency are best determined by the ASTM D97 Pour Point Test, dynamic viscometry, and wax deposition testing (e.g., cold finger and dynamic pipe loop). Knowledge of deposit behavior under differing conditions of temperature and in the presence of different solvent types is critical to devising a plan to remove existing deposits. Once the behavior of waxy crude oils and the deposits they form is clarified, an intelligent and effective means of dealing with them can be devised.

HISTORICAL TREATMENT CONSIDERATIONS

Some of the factors affecting the design of treatment methods include carbon chain distribution, cloud point, pour point, viscosity, solids type and content, melting points, asphaltene content, and physical hardness. Wax deposits may be comprised of several different molecular weight waxes and a variety of non-wax solids (e.g., silt, asphaltene, corrosion byproducts, and inorganic scales). These aggregate solids are extremely difficult to remove with any given treatment methodology, since they are a conglomeration of different materials. The use of heat combined with a wax solvent acting to melt the waxes and disrupt the accumulated deposit is one of the most successful treatment methods. However, with continued heat and solvent treatments the unresolved remnants of the treatment become increasingly hardened and higher melting wax/solid conglomerations. Because the amount of wax that can be held in solution is directly proportional to the temperature and inversely proportional to the wax molecular weight, the higher melting fractions are left behind after heat treatment with oil, solvents, and water.

Hot oiling is frequently done with the crude oil obtained from the very lease that is experiencing the accumulations of wax obstructions. The use of these fluids is not a good idea since it has already shown that it has reached a point of wax saturation by depositing wax in the wellbore, tubing, transfer lines and storage tanks. Hot watering is even more damaging since the water or water/surfactant package has very little, if any, solvency for waxes present in the system. Frequently small amounts of paraffin solvents are added to the production stream, flow line, storage tank, and pipeline to remove pre-existing deposits from these areas. This is a practice that produces little, if any, effect, since the ability of a solvent to dissolve wax is also directly dependent on their concentration in the solvent/s employed. Therefore, it might take ninety percent solvent to dissolve some of the higher carbon chain length paraffin. While paraffin crystal modifiers are most often used to prevent the accumulation of wax deposits and improve the overall handling properties of crude oils, their incorporation into a hot oiling or solvent deposit remediation program can significantly improve treatment results. Since crystal modifiers act to alter the morphology of the forming wax crystals, rendering them less likely to interact, their incorporation into hot oil and solvent packages confers an increased wax carrying capacity to these treatment systems.

Most of the time treatment programs are carried out on systems that have been subjected to hot oiling or hot watering for several years. These programs are handicapped from the start, because of the accumulation of damage in these systems tends to be very extensive. In order to implement a program that will effectively treat the accumulated damage it is necessary to examine what the damage is and what solvent(s), combined solvent(s) and crystal modifier(s) will be required. Samples of crude oil and deposited materials are obtained from various points in the system (e.g., the tubing, transfer lines, storage tanks, and pipeline pig traps) and examined. Melting points and solvency tests are conducted on the solid samples, while pour point and deposit tests are performed on the crude oil. Some wax deposits obtained from wells and flow lines that have undergone years of thermal treatments exhibit melting points well above 200° F, and yield large amounts of sediment when heated in the presence of aromatic solvents. This situation suggests that the continued use of thermal methods will produce no additional benefit unless temperatures are increased, or solvency is enhanced or both. This leaves us with the option of using non-conventional methods (e.g., bacteriological, or magnets), or combining solvents, solvents and surfactants, and solvent and hot oil crystal modifiers.

COMBINATION INORGANIC AND ORGANIC DEPOSITS

Flexibility is very important in the intelligent application of wax deposition control and deposit remediation. If, for example, scale or corrosion byproducts have been found in the deposit, it is perfectly reasonable to include some scale or corrosion control in the treatment. **A** combination scale inhibitor and crystal modifier or a combination corrosion inhibitor and crystal modifier might be called for in the treatment blend(s). Accessibility to deposited matter is of importance when attempting to remove incongruent solids, such as paraffin coated inorganic scales. Incorporation of organic solvents admixed with mutual solvents (e.g., ethylene glycol mono-butyl ether) is effective in stripping organic material from such solids. When applied ahead of an acid treatment, stripped carbonate scales can be contacted by the acid and quickly dissolved. Additional surface disruption benefits may be achieved by co-blending ionic and/or non-ionic surfactants into the blend of solvent and mutual solvent. This can be accomplished through new patent-pending advances in combination product technology. Utilization of this technology allows the combination of products like paraffin crystal modifier, scale inhibitor, organic solvent, ionic and/or non-ionic surfactant, and mutual solvent into a single blend that can be delivered to these troublesome deposits.

Inorganic scales and corrosion byproducts are not the only types of deposits incorporated into growing paraffin wax crystals asphaltenes, emulsions, and insoluble organic salts are often also present. These deposits constitute just as serious a problem as their inorganic solid counterparts, but require different methods of effectively removing them from the system. Asphaltenes are very inert organic macro heterocycles that are most effectively dealt with by suspension micellerization (e.g., break up and inclusion by dispersents into particles of less than 5 microns in diameter). Water-in-oil emulsions and oil-in-water emulsions require demulsifiers in order to resolve tiny water and oil vesicles into two separate, continuous layers. The incorporation of any of these deposit entities into a growing wax crystal makes the task of effectively removing them a more complicated procedure than it would be otherwise. Therefore, designing a treatment program that addresses these problems implies a need to understand the modes of operation of the specialty chemicals that are employed for asphaltene treatment and emulsion resolution. It is also important to realize that accessibility of the asphaltene, emulsion, or organic solid is often key to the successful resolution of the conglomerate deposit. Just as inorganic salts, silts, and corrosion by-products are coated by paraffin and visa versa, so too are asphaltenes, emulsions, and organic salts. The employment of solvents combined with asphaltene suspending agents, emulsion breakers, and dispersents is necessary to assure accessibility to the problem species. Further, the incorporation of paraffin crystal modifiers into this admixture insures that the continued process of aggregation and networking of the waxes is impeded, and inclusion in or by other deposit components is effectively reduced.

SOLVENT CONSIDERATIONS

The selection of solvents that are useful for the removal of wax deposits is not a simple matter. In the not too distant past exotic solvents, such as carbon disulfide, sulfolane, and benzothiophene were employed as treatments for wax deposits, but legitimate health and safety issues surrounding them have curtailed their use. The process of dissolving wax and combined waxy solids requires a careful examination of the behavior of these deposits in a variety of solvent systems. Crude oil or condensates, which are often applied by hot oil trucks, are the most widely used solvents for organic damage removal. Water and surfactantlwater combinations applied with or without heating comprise the second most frequently encountered treatments, while aromatic and aliphatic solvents comprise the third most widely used categories of solvents. The wax carrying capacity of the various solvents is inversely proportional to the molecular weight of the waxes, the polarity of the solvent, and amount of solvated wax, and is directly proportional to the temperature. When asphaltenes are present as part of the deposit, aromatic solvents exhibit superior dispersent properties, especially when asphaltene dispersent chemicals are included. The presence of water as emulsion or as a film on surfaces adds to the difficulty of solids removal. Ionic or non-ionic surfactants combined with mutual solvents and organic solvents act synergistically to increase accessibility to the organic portions of the deposit. Empirical results obtained from field or laboratory solvency tests are necessary in order to make the proper choice of solvents and combined solvent/surfactant treatments.

TREATMENT DESIGN

Field treatment history is of prime importance when designing a program for future treatments. Additional information such as production rates, deviations from expected natural production decline, hot oiling or watering frequency, solvent treatment frequency, work-over frequency, pigging frequency, tank bottoms treatment frequency, etc, are important if not essential. When this type of information is combined with pertinent analytical testing results from crude oils and deposit samples, a powerful tool for devising effective treatment strategy results. Historical and analytical data are not sufficient in themselves. Additional testing on the physical behavior of the crude oil is necessary. Results obtained from pour point tests, deposit tendency tests, viscosity tests, and crystal modifier tests add to the utility of the information. Additionally, data obtained in the laboratory about the effects of solvency, heating, demulsification, asphaltene suspension, salt and silt dispersion, and solid sample behavior in acid are of great utility when dealing with existing deposits. Organic and combined organic/inorganic depositions are vastly more complicated than straight inorganic scales, and the methods of dealing with them reflect that complexity. Straight inorganic scales are very frequently pure substances like calcium carbonate, calcium sulfate, barium sulfate etc., whose crystal habits can be altered by the incorporation of very small amounts of inhibitor. While organic paraffin wax crystals may be a combination of several different molecular weight waxes, or carbon chain length species that form a spectrum of macro-aggregates, and require a variety of crystal modifier variants. Thus, organic deposit control often requires a much higher level of chemical treatment than do pure inorganic scales.

In cases where years of damage have been accumulated and deposits are comprised of several organic and inorganic components, the application of small amounts of solvent over-flushed with large volumes of lease crude or water has minimal, if any, effect. These situations call for an amount of solvent, or dry lease crude, combined with other surface-active components sufficient, to cover the production interval. Heating, if possible, will nearly always aid in the resolution of these deposits, but if heating involves a danger of fire or explosion, safety should always be of paramount concern. Hot oil trucks can provide a valuable service if the oils or solvents they pump contain crystal modifiers to alter the wax crystal behavior of the oils used. Some applications require a treatment with solvent followed by acid to remove scale build-up, but newly developed combined multi-component systems provide an advantage to this staged approach. If combined products containing scale inhibitor, wax crystal modifier, emulsion breakers, and solvent contact these deposits, the deposits will be removed or altered making them less likely to recombine in the system.

FIELD CONSIDERATIONS AFFECTING TREATMENT

A common misperception in the oil field is that crude oils that exhibit very low pour point temperatures (e.g., -30° F) do not produce wax deposits. Although crude oils may pour at very low temperatures, they can still produce major deposits in wells, flow lines, storage vessels, and pipelines. The reason deposits occur when elevated pour points are not observed is that the wax networking throughout the oil is interrupted, and the concentrations of wax species bridging the range of molecular weight from high to low are negligible. This means that high molecular weight waxes may be present, but they cannot combine with intermediate molecular weight waxes to cause the oil to gel. Thus, the volume of crude oil that has been produced and the concentration of higher molecular weight wax it contains determine the type and quantity of deposit observed. Since crystal modifier applications in the oil field have been slow to develop, many producers are unfamiliar with their function, and question whether they are useful or not. However, crystal modifiers are necessary, and had they been employed from start-up and continued throughout production the necessity for clean ups would have been drastically reduced.

Economic factors, competitive pressures, and operator cost constraints provide compelling reasons to minimize the costs of these treatments. However, the insistence on low initial treatment costs has led to long term problems that have required expensive remediation measures that are more costly in the end. In many of these cases, the old adage "An ounce of prevention is worth a pound of cure", could not be more appropriate. Continued pressure to provide the lowest cost treatments has led to the implementation of remediation programs that are, at best, ill advised and are, at worst, destructive. Many people will agree that "healthy competition" is what leads to progress, but it is doubtful that many will agree that product quality should be sacrificed to win that competition. It is, or at least should be the responsibility of the provider of a product to insure that product is of sufficient quality to perform as expected by the customer. When competition has become "unhealthy" due to unreasonable or unachievable demands made by customers, the provider of a product has a duty to tell that customer. He or she should not, for the sake of profit, sacrifice minimum product quality or utility.

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