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UNIQUE NATURAL SOLVENTS FOR TREATING PARAFFIN AND ASPHALTENE RELATED PROBLEMS

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Abstract:

Problems related to paraffin and asphaltenes continue to plague the oil and gas industry. These include solid deposits, stabilization of emulsions and sludge production[1-4]. Common solvents and condensates are popular treatments for dissolving and/or controlling paraffin and asphaltene related problems. Typically, these fluids have been used with little regard for long term effectiveness and formation damage consequences.

Unique condensate feedstocks with high multiple aromatic content were identified. Laboratory testing, blending and refining resulted in solvents that can keep paraffin and asphaltenes in solution under a wide range of conditions. As a result of this work condensates are blended and refined to maximize solvency, demulsifying properties and maintain wettability without the addition of chemical additives. The properties of these refined natural solvents offer economical alternatives and/or enhancement to common treatment practices including hot oiling, condensate treatments, chemical treatments, stimulation and production treatments.

Introduction:

Crude oil is exposed to thermodynamic changes during production, storage, transportation and refining. These changes will adversely affect the crude oil chemical equilibrium changing the physical properties. These changes will most likely induce paraffin crystallization and/or asphaltene flocculation and precipitation. Research and product development has been historically directed toward inhibiting paraffin and asphaltene precipitation with little attention being given to developing or enhancing hydrocarbon solvents. Many chemicals and solvent blends exist that prevent or inhibit paraffin and asphaltene precipitation but most are crude specific. Individual testing and compatibility with the formation, reservoir fluids and treating fluids must be considered. Typically, the introduction of incompatible fluids, gases and chemicals into the reservoir is the main cause of damage and the resulting loss of production. Almost any change in equilibrium can potentially cause organic deposition and reduce permeability. Although a number of physical and chemical events can change the equilibrium, the most common are categorized as follows: (1) Cold fluids can precipitate paraffins. This occurs when the oil is cooled below the cloud point. In some instances there is insufficient formation heat available to dissolve the precipitated paraffin. (2) An acidic shift in pH can cause asphaltene precipitation and sludging. This typically occurs during acid treatments and when CO_2 combines with formation water in CO_2 floods. (3) Strongly charged chemicals may change natural wettability. Strongly cationic chemicals may oil wet a sandstone and strongly anionic chemicals may oil wet a carbonate formation. (4) Pressure drops and the resulting shear and temperature drop. (5) Even the introduction of heated oil to dissolve deposits is known to cause formation damage[2].

Quite often these deposits and formation damage are labeled as a paraffin or asphaltene problem. However, deposits can contain resins, gums, crude oil, water and inorganic matter in addition to paraffin and asphaltenes. It is beyond the scope of this paper to review the detailed chemical and physical properties of paraffin and asphaltenes. Paraffin is assumed to be straight or branched chain alkanes represented by the general formula C_nH_{2n+2}. These hydrocarbons are essentially inert to chemical reactions and are therefore resistant to attack by acids and bases. They do have specific physical and chemical properties, the most important being a specific cloud point and melting point. Asphaltenes on the other hand are normally polar because of the presence of oxygen, nitrogen, sulfur and various metals in the molecular structure. Asphaltenes are typically $C_{70}+$ macromolecules with no specific chemical structure. Only a statistical average structure is known. They are colloidally suspended by gums, resins and maltenes as peptizing agents. When these compounds are removed or diluted, the polarized asphaltene molecules flocculate and/or precipitate. The ratio of paraffin, asphaltenes, gums, resins, free oil and other matter can vary greatly from surface samples to deposits in the wellbore or even in the formation. Hence, a solvent should have the ability to dissolve, disperse and suspend these compounds in varying ratios.

Considerable quantities of condensates are used for paraffin treatments. They are used alone and as a carrier fluid for chemical dispersants and inhibitors. Many of the chemicals have xylene, toluene, naphthas or condensates as the base fluid. In many instances it is erroneously accepted that any solvent or condensate will work, especially if it is inexpensive. This practice is apparent from the variety of condensates and refined solvents used including xylene, toluene, heavy aromatic naphthas and the almost endless variety of condensates. This is compounded by naphthas being substituted for or sold as xylene or toluene in some instances. Condensates and refined solvents are used individually or blended[3] to maximize solubility and effectiveness. Although considerable volumes of condensates are used, little research has been directed toward detailed condensate component identification and potential product derivatives.

The volume and apparent effectiveness of condensate treatments led to an investigation of condensate properties. The investigation was divided into two categories: (1) Identify any damaging or undesirable components or properties. (2) Identify the non-damaging and desirable components and properties. The desirable properties include the ability to dissolve a wide range of paraffin and asphaltenes, maintain natural wettability, non-emulsifying and compatible with the formation and reservoir fluids. Additionally, the fluid should minimize or eliminate disposal problems and be economical.

Theory and Test Summary:

Three primary screening and testing methods were chosen to evaluate condensates. Aromatic content, solvency performance and emulsion tests were the primary focus. Once the most effective condensates were identified then wettability tests were performed.

Condensates from many sources were analyzed using chromatography to identify specific compounds present. It is well documented that low carbon chain hydrocarbons, less than C_7, precipitate asphaltenes. For example: In the laboratory, n-pentane, C_5 or n-hexane, C_6 is commonly used to precipitate asphaltenes. Additionally, any organic hydrocarbon with a surface tension of less than 24 dynes/cm will precipitate asphaltenes[4]. This includes most condensates, gasoline, naphthas and diesel. Light condensates typically contain compounds starting as low as C_4. Gasoline contains C_4 through C_{12} compounds. Naphtha components range from C_5 through C_{10}. Diesel does not contain any base molecules lower than C_5 but it does contain additives. These additives can lower the surface tension to 24 dynes/cm or less and often have a tendency toward oil wetting.

Figure 1 shows a chromatograph of a 60 API gravity condensate from southern Oklahoma. The volume below C_7 is 34%. Although this condensate could be very good for dissolving paraffin it will precipitate asphaltenes. It has a low surface tension and has a considerable volume of C_4 through C_6 components.

Using the pentane insoluble test, a central Oklahoma crude was shown to contain 1.72% pentane insolubles or asphaltenes. Repeating the procedure using the condensate in place of the pentane, 1.86% insolubles were recorded. Additional tests were run with different crude oil and stock condensates with similar results. Significant levels of asphaltenes were precipitated even when the condensate contained minimal amounts of C_1 to C_6 components. With this knowledge it is apparent that any solvent derived from condensate feed stocks would require all C_1 through C_6 hydrocarbons removed. Removal of the damaging components would potentially result in a fluid that is universally compatible with all crude oils.

A Distillation process to remove all components from C_1 through C_6 and any components higher than C_{13} from condensates and light gas oils was developed. After removing these components, the remaining C- to C_{13} fluid was tested. Separate testing for dissolving paraffin and asphaltenes was conducted. Once condensates with the highest solvency were identified, non-emulsifying and wettability tests were completed. Detailed chromatograph analysis was performed to identify specific aromatic compounds present.

The selection, blending and refining of specific condensate feedstocks resulted in two solvents. These are identified as solvent "W" for dissolving paraffin or wax and solvent "X" for dissolving asphaltenes. Both solvents are petroleum distillates having components between C- and C_{13}. Although this is a relative narrow range of total carbon atoms, two very separate and distinct solvents were blended.

The ability to have two distinct products over a narrow carbon number range is due to the number of aromatic and naphthalene molecules possible. Hundreds of naphthene molecules are possible with a carbon number of C- through C_{10} and hundreds of different aromatic molecules are possible between C- and C_{10}. Solvent W has a specific gravity of .80 and an aromatic content of 59% and solvent X has a specific gravity of .87 and aromatic content of 84%. Although specific composition is proprietary it is apparent solvent W has more light components than solvent X.

A high percent aromatic content does not automatically provide the most dissolving capability. This is evident in that xylene and toluene are both 100% aromatic but solvating performance will vary depending on the specific paraffin or asphaltene. Two methods of solvency testing were performed. The first method was a comparison to hot toluene. In summary, a 1 gram sample was washed with 1,000 to 2,000 ml. of toluene heated to 212°F. and the percent dissolved calculated. A 1 gram sample was then placed in 100 ml. of the test solvent and let stand for 1 hour with periodic agitation. The percent dissolved was calculated and compared to the hot toluene value. For example a sample from the Hart formation in S. Central OK was 89.8% dissolved with a hot toluene wash. The sample was then tested in solvent W at room temperature. In one hour 87.8% of the sample dissolved at 70°F.

Another test method involved dissolving an equal weight of solid sample in equal volumes of different solvents. The solvent and sample solution were heated to reservoir temperature, held at that temperature for a specific interval then allowed to cool to room temperature. Each was filtered and the dissolved percentage calculated. A sample containing 36.4% paraffin and 3.1% asphaltenes was tested using this procedure. The percent dissolved by three solvents is as follows: Xylene = 50.3%, Solvent W = 56.7% and solvent X = 57.9%. In some instances the saturated solvents were cooled to simulate cold weather production circumstances. In most cases the xylene solution increased in viscosity and solidified before solvents W and X. The natural solvents have complex aromatics that act as crystal modifiers and peptizing agents keeping paraffin and asphaltenes dispersed, suspended and in solution. Natural solvent field applications of 20% to 50% less volume in place of the refined single aromatic solvents such as xylene and toluene have performed as well or better.

The Kauri-butanol (KB) value of hydrocarbon solvents is often used for evaluating or choosing a solvent. In some instances it is the sole determining factor for field use. The KB value is a measure of solvating ability using Kauri resin from the Kauri Pine as the defined standard. The test originated in the paint and lacquer industry and the higher the KB value the higher the relative solvating ability. Paragraph 1.1 of ASTM-D-1133-90[3] Standard Test Method for Kauri-Butanol Value of Hydrocarbon Solvents states: "This test method covers the determination of the relative solvent power of hydrocarbon solvents used in paint and lacquer formulations". i.e.: Hexane has a KB value of 30.5, Heptane has a KB value of 30.0, Xylene has a KB value of 98, Toluene is KB = 105 and benzene has a KB value of 107. Since each of these can perform superior to the others in different applications the KB value is not an absolute indicator of solvency for oilfield applications. The compatibility with the formation, reservoir fluids, ease of disposal and cost effectiveness have as great if not more importance than the specific KB value.

Treatment Applications:

It should be noted that many times the treatment technique is more important than the dissolving power of the solvent. Where formation pore spaces are partially plugged with paraffin and asphaltenes the volume of solvent that can be injected into the pore can be extremely small when compared to the mass and surface area of contact. In these instances it is more practical to design several smaller treatments than one large all or nothing treatment.

These natural solvents can be added to conventional treating techniques. They can be added at a ratio of 10% by volume to hot oil treatments. The hot oil will dissolve the lower end paraffins and the solvent is then available to soften and dissolve the higher melting point paraffins. The same principle applies to the use of hot water treatments as well. A ratio of 1% to 10% by volume will soften and dissolve the higher melting point paraffins.

Although condensates should not be injected into the formation it may be economical and practical to use them as flush volumes. Injecting 5% to 20% of the refined natural solvents in front of the condensate treatments can greatly enhance the performance. The condensate will wash all the solvents to bottom and provide a diluting fluid to the paraffin saturated production. Care should be taken to not overflush where the condensates can precipitate asphaltenes in the formation.

Field Results:

Case History: (Hot oil additive)

An oil storage tank containing 200 Bbls. of oil was not acceptable for sale. A thick layer of paraffin had formed on the top and a high water content in the lower portion was reported. A hot oiler was used to heat the tank and circulate 100 gallons of solvent W into the oil. The paraffin layer was dissolved and held in solution when the oil cooled. The paraffin stabilized emulsion was broken and the oil was ready for transportation and sale.

Case History: (Hot oil replacement)

This well is a 7,200 ft. well in South Central Oklahoma. The wellhead oil sample contained 16.1% paraffin and 1.2% asphaltenes. Historically, it required hot oiling every 30 days. During the period of 1991 through August, 1993 the average daily production was 15 BOPD. At the end of August, 1993, 350 gals. of Solvent W was pumped into the annulus. The tubing was connected to the annulus and the downhole pump used to circulate the well for 24 hours. The well was returned to production. The production during September of 1993 averaged 24 BOPD. The monthly hot oil treatments were replaced with a batch treatment of 80 gals. solvent W each month. To date the well is still averaging over 20 BOPD.

Case History: (Acidizing additive)

This New Mexico well is in a CO_2 flood and was known to have paraffin, asphaltene and scale deposition. The eight months prior to an acid/solvent treatment the well averaged 30 BOPD, 269 BWPD and 302 MCFGD. An acid treatment was performed using 25% by volume of solvent X chemically dispersed with the acid. The six months of production after the treatment averaged 62 BOPD, 120 BWPD and 787 MDFGD.

Conclusions:

1. Specific condensate feedstocks can be blended and refined into formation and reservoir fluid compatible solvents.

2. Refined multi-aromatic condensates will perform as well or better than single component aromatics such as xylene and toluene.

3. Refined condensates used in stimulation treatments will enhance production where paraffin and/or asphaltenes are a problem.

4. Natural solvents can enhance and be an economical enhancement to

conventional paraffin and asphaltene treatment methods.

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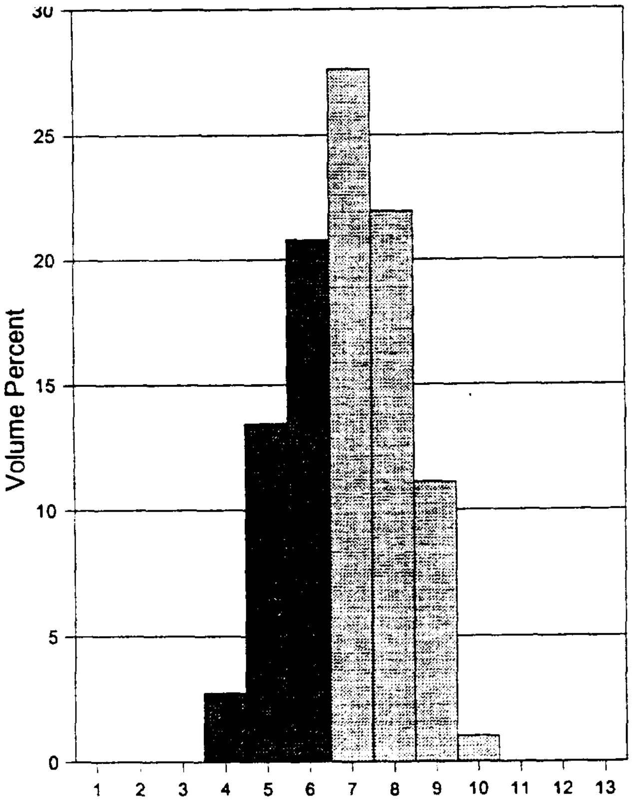

Figure 1 - Total Carbon Number - 60 API Gravity Condensate