Paraffin Deposition and Prevention in Oil Wells

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THE CHEMISTRY OF PARAFFIN

The problem of paraffin deposits in producing oil wells is one of long standing.[1] Paraffin deposits are troublesome and costly because masses of paraffin precipitate and cling to sucker rods, tubing, and flow lines effectively reducing the size of the flow conduit, and requiring removal. In the terminology of the organic chemist, paraffins are any of a homologous series of saturated hydrocarbons following the structural formula $C\ H_2\ {}_{+2}$, where "n" is an integer.[2,3] All of the following are paraffins:[3]

Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Octadecane	$C_{18}H_{38}$

In oil field terminology, however, the "paraffins" are only those hydrocarbons which have sufficient molecular weight to possess the property of being a solid at operating temperatures. This is similar to certain industrial terminology which describes paraffins which are solid at room temperature as waxes.

In oil field operations, the paraffins which are troublesome (i. e., solids at operating temperatures) are hydrocarbons ranging from about $C_{18}H_{38}$ to $C_{38}H_{78}$. These have usually been found to be principally composed of mixtures of straight chain hydrocarbons, although small amounts of branched chain and aromatic constituents have been identified in paraffin samples recovered from producing wells (Fig. 1).

The melting point of any normal (straight chain) paraffin increases as its molecular weight increases. An n-$C_{18}H_{38}$ paraffin has a lower melting point than a normal paraffin of the composition $C_{38}H_{78}$. In practical terms, this means that a higher temperature must be used when "hot oiling" to remove paraffins averaging $C_{38}H_{78}$ in composition than the temperature necessary to melt $C_{18}H_{38}$ compounds.

Solubility of paraffins in crude oil or other paraffin solvents decreases as the molecular weight of the paraffin increases. The solubility of $C_{18}H_{38}$ in non-polar solvents is several times that of a high molecular weight paraffin such as $C_{38}H_{78}$. Again, in practical terms, a $C_{38}H_{78}$ paraffin would require a greater volume of any given solvent than would a $C_{18}H_{38}$ paraffin during paraffin removal from an oil well.[3]

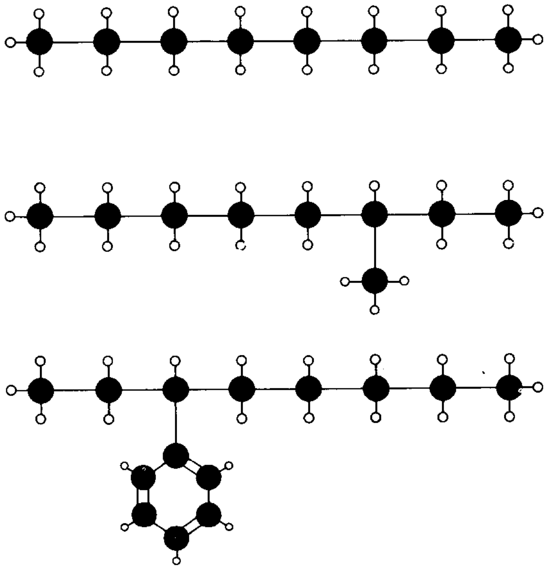

Fig. 1 - A straight chain paraffin (upper), a branched chain paraffin (middle), and a paraffin containing an aromatic side chain (lower). Black circles are carbon atoms, open circles are hydrogen atoms.

Knowledge of the composition of troublesome paraffins can be an important asset when prescribing removal treatments. The small cost required to have a local laboratory obtain paraffin composition and melting range from a representative sample of paraffin can often provide information which will mean the difference between efficient paraffin removal and haphazard operating practices.

Paraffins are non-polar materials.[2,3] This means that they are not selectively adsorbed onto any surfaces, and that forces other than chemical attraction are required to cause paraffin deposits in oil wells. The non-polar property of paraffins accounts for the fact that non-polar solvents are better paraffin solvents than are polar solvents.

The following listing compares solvent effectiveness with the polarity of the solvent.

Chemical Name	**Formula**	**Effectiveness as Paraffin Solvent**
Gasoline (Non-polar)	C_7H_{16}	Good
Carbon Disulfide (Non-polar)	CS_2	Good
Ethyl Alcohol (Polar)	C_2H_5OH	Poor
Methyl Ethyl Ketone (Polar)	$CH_3COC_2 \cdot H_5$	Poor
Carbon Tetrachloride (Non-polar)	$CC\ _4$	Good
Toluene (Non-polar)	$CH_3C_6H_5$	Good

Generally, compounds containing oxygen or other electron-withdrawing atoms or groups of atoms are polar, and thus are not as effective as non-polar compounds for dissolving paraffins.[3]

The last item dealing with the chemistry of paraffins concerns the nature of the paraffin deposits as they are found in oil wells. Groups of individual solid paraffin molecules collect and join to form crystals, which in turn are joined to other crystals to form what appears to be a solid mass of paraffin. Actually, the paraffin which deposits in oil wells is an irregular lattice of connected paraffin crystals, with all of the space between all the crystals occupied by produced crude oil and water.[4]

THE MECHANISM OF PARAFFIN DEPOSITION IN OIL WELLS

An example oil well, the model used for this discussion, is shown in Fig. 2, and should be referred to frequently during this section of the text.

The model exhibits orderly temperature behavior; during production of the well the oil stream is constantly being cooled because of heat loss from the tubing and flowline, and has highest temperatures in the reservoir and lowest temperatures at the end of the flowline. For the purpose of illustration, typical but arbitrary tem-

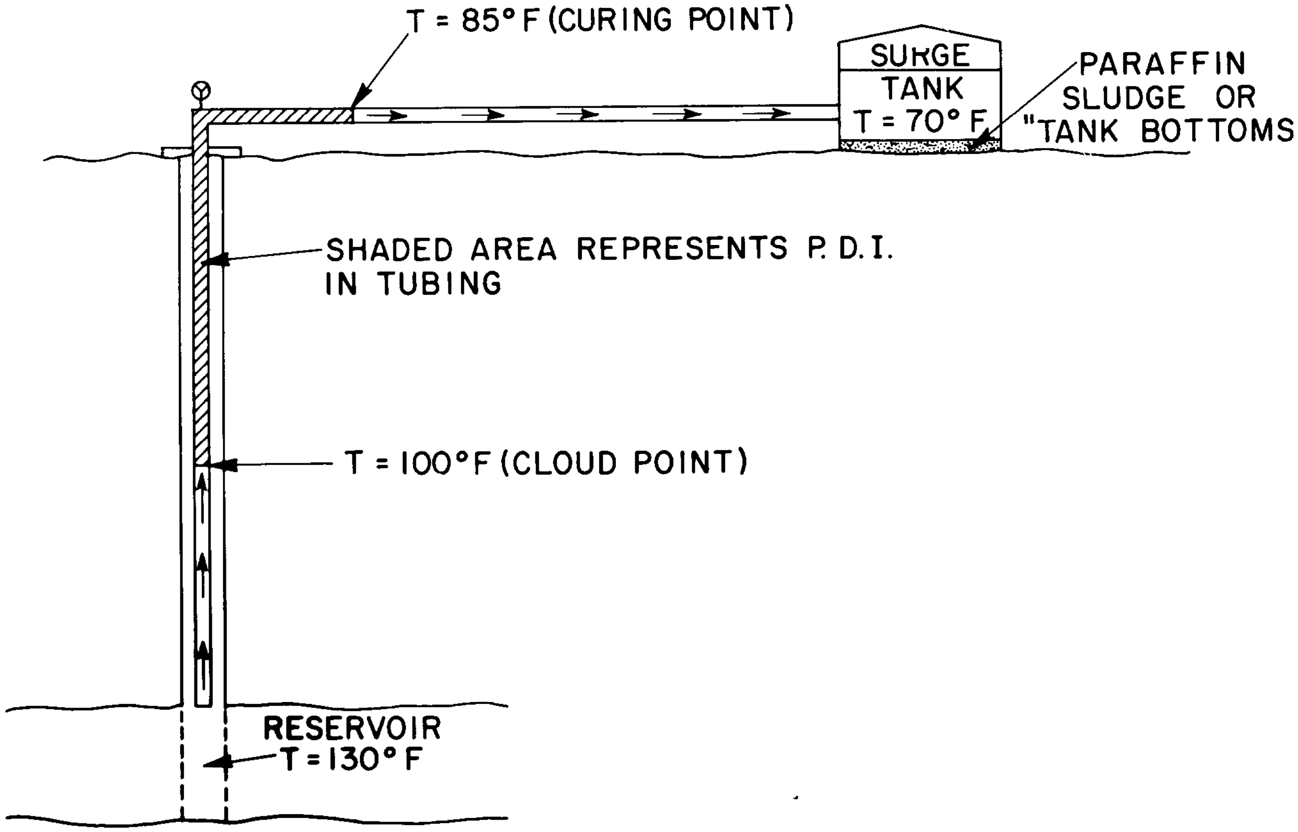

Fig. 2 - Flowing oil well model referred to in text.

peratures have been assigned at significant intervals in the model well. Three terms must be defined before proceeding. They are:

(1) **Cloud Point** — the temperature of any given crude oil at which paraffin is no longer soluble in the crude oil; otherwise stated, it is the temperature at which paraffin molecules change from liquid to solid state.

(2) **Curing Point**— the temperature at which precipitated collections of paraffin molecules no longer possess the property of adhesion (no longer "sticky").

(3) **Paraffin Deposition Interval**—the limits in an oil well conduit system in which the temperature of the oil stream is (a) below cloud point and (b) above the curing point.

Paraffin is known to deposit (adhere to the metal) in oil wells only in the Paraffin Deposition Interval (PDI). At temperatures above cloud point (upstream of the PDI), paraffin is always in solution. At temperatures below the curing point (downstream of the PDI), paraffin is no longer sticky and, though it exists as a thin film on the walls of the conduit and as a sludge in the flow stream, it does not build up on the metal in the system.[4]

The mechanism of paraffin deposition on metal and other surfaces has been demonstrated to be one in which (1) the oil stream reaches cloud point, (2) accumulations of paraffin molecules (crystals) are mechanically trapped on the rough metal surfaces, and (3) other paraffin crystals, because they are still in an adhesive state, are attached to the paraffin crystals which are trapped in the surface irregularities and build into a continuous layer. There is no other explanation which fits all of the facts gathered in laboratory and field tests.[4]

The roughness of the tubing wall appears to be the principal factor governing the severity of paraffin deposition within the PDI. In fact, all other conditions constant, rough surfaces collect more paraffin, with a higher paraffin content and of a higher molecular weight, and with greater adhesion to the surface than that deposited on smoother surfaces. The relationship is approximately linear; a surface twice as rough as another will result in paraffin deposits about twice as severe in any given PDI.[4]

PHYSICAL MEANS OF REDUCING PARAFFIN DEPOSITS

The importance of the PDI concept and the dependence of paraffin buildup on surface roughness has led to an understanding of physical means to minimize paraffin deposition in oil wells, namely, the use of smooth plastic coatings on tubing and flowlines.

A few years ago, the use of plastics received opinions ranging in spectrum from complete success to dismal failure. Numerous examples of both types could be found in oil field operations. The reasons for the extremes of success and failure are now understood. To preface the explanation, the following characteristics of the three most widely used oil-field plastic coatings are set forth.

(1) **Phenol-formaldehyde**—the most widely used, and the oldest in oil field tubulars. This is a highly cross-linked polymer, with excellent resistance to temperature, chemicals, and infusion by small molecules (H_2O, CH_4 H_2S).[3] The surface is extremely smooth and has a high gloss. This is a brittle plastic and deforms very badly when abraded by sand, becoming extremely rough.

(2) **Epoxy Phenolic**—the second most widely used material in oil field tubulars. This polymer has less resistance to temperature, chemicals and infusion than phenol-formaldehyde.[3] Its surface is almost as smooth as phenol-formaldehyde, but it is less brittle and does not deform so badly as phenol-formaldehyde when abraded by sand.

(3) **Polyurethane**—a relative newcomer, and the least cross-linked of the three. It has lower temperature, chemical and infusion resistance than the other two. This plastics surface is not quite as smooth as phenol-formaldehyde. Polyurethanes are quite flexible, and while film thickness is reduced (as with the other two) by sand abrasion, the plastic is only very slightly deformed and maintains most of its smoothness.

With these descriptions in mind, it is somewhat apparent why plastics behaved so well or so poorly, depending on the experience of the particular oil operator. In areas where the oil stream did not contain sand or other abrasive solids, plastics did a good job preventing paraffin buildup. Where brittle plastics, such as phenol-formaldehyde, were used and where the wells contained abrasive materials, the plastic was badly deformed. Because of the resulting extreme surface roughness, after the plastic became abraded, severe paraffin deposition occurred.

Once the importance of surface roughness was recognized, oil operators relied on the resilient polyurethanes (at some sacrifice in resistance to temperature, etc.) where the well streams contained abrasives, and used the more temperature-resistant, phenol-formaldehyde or epoxy-phenolic materials where the oil was free of abrasives.

Four other noteworthy statements can be made regarding the use of plastic coatings to prevent paraffin deposition.

(1) Paraffinic plastics such as polytetrafluoroethylene, polyethylene and polypropylene, no matter how smooth, will not reduce paraffin buildup. In fact, because they are paraffins themselves, they cause paraffin buildup due either to hydrogen bonding, or to a phenomenon closely resembling co-crystallization.[4]

(2) Smooth, non-paraffinic plastics reduce paraffin deposits only as long as they remain smooth. Wire lines, fishing tools, piano wire equipment and other workover or measuring devices destroy the effectiveness of the plastic coating by damaging the smooth surfaces.[4]

(3) **All** metal surfaces (nipples, valves, etc.) in the PDI must be coated with plastic. One uncoated nipple can effectively choke the well. It is good practice to extend plastic coating about 100 feet on both sides of PDI.

(4) The PDI will vary when flow rates are varied. Also, the curing point will be altered by outside air temperature if the curing point is located in a surface flowline.

PARAFFIN CONTROL WITH CHEMICAL INHIBITORS

It has long been desired to inhibit paraffin deposition by injecting continuous, small (about 100 parts per million) amounts of chemical into the oil stream upstream of the PDI by injecting the chemical through the tubing-casing annulus to the well bottom. The chemicals tried were usually (1) anionic organic materials, (2) cationic organic materials, (3) non-ionic organic materials, or (4) aromatic compounds. In no case has widespread use of any broad-spectrum chemical been successfully reported.

Historical opinions suggest that in order to inhibit paraffin deposition, a chemical must (1) stop the growth of the paraffin crystal, or (2) reduce the adhesive tendency of the paraffin crystal, or (3) alter the surface properties of the paraffin crystal, or (4) impart a paraffin-repelling property to the deposition surface, or (5) combinations of (1), (2), (3), and (4). Whereas small, continuous doses of certain chemicals do an effective job of controlling corrosion in oil wells, the same cannot be said about paraffin control chemicals. Usually in corrosion control, chemicals are used to stifle electron flow, and it follows that low part-per-million doses of selected materials can effectively accomplish this. Calculations show, however, that the total surface area of precipitating crystals of paraffin is so large, even in low paraffin content wells, that administering low part-per-million quantities of even the best of chemicals cannot be very successful. The literature contains many articles related to this subject. A reasonably accurate summary of the effectiveness of chemicals in reducing paraffin deposits was recently set forth in what now appears to be gaining popularity as the "Abe Lincoln" description.

> Some chemicals inhibit some paraffins.
> Some chemicals inhibit no paraffins.
> No chemicals inhibit all paraffins.

On the basis of surface area calculations (not presented in this text), it can be said with reasonable assurance that, in order to be effective as a paraffin inhibitor, a chemical will have to be found which uses a principle other than (1), (2), (3), (4), or (5) delineated in the preceding paragraph.

The most attractive new prevention principle observed to date is contained in the scantily-reported use of polyethylene granules, which appear to work because the granules provide preferential sites for paraffin deposition, and after having preferentially collected the paraffin, are transported up the well as a sludge.[5] This is the first new theory which has been advanced in this field for many years.

Other evidence notwithstanding, the most sound recommendation which can be made at this time is: if there is no other alternative to chemical inhibition of paraffin, let controlled field tests provide an answer, being aware that success may not be attainable.

COMMON PARAFFIN REMOVAL PRACTICES

Up to this point, this text has been directed to paraffin chemistry, deposition, and prevention methods. It should be obvious that paraffin removal techniques may be needed if (1) the expense of plastic coating cannot be justified; (2) paraffin inhibitors either do not work or are too costly. Paraffin removal techniques are much older and more thoroughly proven than are paraffin prevention techniques. Most are well known to oil operators, and are listed here (not necessarily in order of effectiveness) for review purposes.

Production Methods

The use of a back-pressure regulator to prevent loss of light ends is often helpful. Keeping a vacuum in the tubing-casing annulus reduces heat loss in the tubing and may keep the oil stream temperature above cloud-point. The use of small tubing to reduce heat loss by reducing travel time of oil from the reservoir to the tank may help.

Mechanical Methods

This group includes wire line scrapers, sucker-rod mounted scrapers, the paraffin knife, the paraffin hook, and a variety of such devices.

Hot Fluid Application

Various hot petroleum liquids, hot gas, steam, and hot water are used to melt and/or dislodge paraffin.

Electrical Heating

Various electrically powered heating elements are available at this writing.

Chemical Heating

Some operators have successfully used materials which undergo exothermic reactions to generate heat.

Solvent Methods

Chemicals in which paraffin is highly soluble are often used to remove the paraffin by solution processes. Often these solvents are heated to combine the benefits of both methods. Caution must be used when employing such materials as carbon tetrachloride (poisonous fumes) or carbon disulfide (extremely flammable).

EXPLOSIVE METHODS

Explosives such as trinitrotoluene (TNT) and glyceryl trinitrate (nitroglycerine) have been used to clean wax from the sand face. The explosion raises the temperature and physically helps dislodge the deposits simultaneously.

MAGNETIC SUBS

Although such devices are sold for paraffin prevention, it is somewhat difficult to understand how a non-polar compound such as paraffin can be oriented by a magnetic field, or what effect such orientation, if possible, would produce.

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