# COLD FINGER TESTING – THE GOOD, THE BAD AND THE UGLY

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## ABSTRACT

The Cold Finger Test is the primary test presently used by Chemical Vendors to select Paraffin Inhibitors to prevent paraffin deposition in producing gas and oil wells, gathering systems, treating facilities and pipelines. If a good Test procedure is used to erase the thermal history of the crude sample to be used and it reproduces the system Temperatures in the area to be treated an effective chemical will be chosen for that system's paraffin problem. Unfortunately, the economic conditions that have befallen the Industry in the past few years have caused both vendors and oil companies to look for short cuts to allow for more to be done with less. Cold Finger Tests are being done with less oil, larger temperature differentials between the oil temperature and the probe temperature and shorter test run times. The use of these short cuts makes more chemicals look good on the test, giving great % inhibition results that many times are not representative of how the chemical will perform in the system. This paper will discuss good test procedures, bad tests procedures and how oil companies need to determine if the results they are getting make sense and have a good chance of solving their paraffin problems.

## INTRODUCTION

The cold finger test in various forms is at least 50 years old. The first test, I know of, from 1966 was described by the following "are contained in a publication by Hunt who developed the "cold spot tester", a really useful means of investigating paraffin deposition. Hunt's observations led to many generalized conclusions concerning the effect of surface roughness on paraffin deposits. He ascertained that there was an observable qualitative correlation between the severity of paraffin deposition and the roughness of the surfaces which he tested (cold rolled steel, stainless steel and several plastics). Because of the number of meaningful observations made by Hunt, his cold spot tester was modified somewhat and extensive tests were performed to study the quantitative relationship between surface roughness and the physical and chemical nature of paraffin deposits. The cold spot test apparatus consists of a flat circular plate mounted on a curved tube and positioned in a vessel containing a wax-oil solution. The apparatus is arranged so that the temperature of the central portion of the circular plate can be varied by means of a circulating liquid stream; the test equipment includes provisions for maintaining a constant wax-oil solution temperature and stirring speed. In the paraffin deposition studies, the modified cold spot tester was used as follows. The cold spot probe consisted of a flat circular plate, 2 in. in diameter and 1/8-in. thick positioned in the wax-oil solution kept at constant temperature. As in Hunt's earlier experiments,' a cold liquid was circulated through a tube connected to the circular plate so that the liquid impinged on one side of the plate cooling the plate from the center outward, causing paraffin to deposit on the side of the plate exposed to the wax-oil solution."[1]

Another test was the spinning disk test reported in a paper in 1976.[2,3] This device used a spinning disk with an electric generated cold metal surface to get deposition from oil. Another device based on the spinning disk used this same method to get deposits of paraffin but was screwed into the bullplug of a well and could get deposits under system conditions in a short period of time. In the 1980's a cold finger test was developed by an oil company and information about the test was spread throughout the industry. This test consisted of a stainless steel probe chilled with water from a cooling bath. The probe was placed in a heated sample of stirred oil for several hours until a paraffin deposit formed on the probe. Procedures for running the test were never standardized so it was left to individual companies to develop their own test procedures. Chemical vendors starting using the test to test chemicals to determine their ability to inhibit paraffin deposition on cold metal surfaces. The cold finger test procedure has never been standardized by an accredited testing organization so companies that run the test can vary any conditions as they see fit. This lack of a uniform (scientific) test procedure has led to tests that can be run quickly with small quantities of oil but may make numerous chemicals give good inhibition results but do not stop paraffin deposition in the system when applied. This gives the oil companies a quick recommendation which they desire, the chemical vendors a low cost test that appears to give good inhibition results but a chemical that may not work in the field.

Answers Immediately, Correct Answers Take Longer!

## PARAFFIN CHEMISTRY

Paraffin in oil and condensates consists of n-alkanes from methane $CH_4$ (Melting Point -296ºF (-182ºC)) to > Hectane $C_{100}H_{202}$ (Melting Point 239ºF (115ºC)). All of the paraffin for any oil is dissolved in the oil at formation temperatures and pressures. No two oils contain the same amounts of the various paraffin present, even wells in the same field will have varying amounts and types of paraffin. The distribution of the paraffin in an oil can be determined using a High Temperature Gas Chromatograph (HTGC).[4] The paraffin stays in solution in the oil until the formation is penetrated by a well and production starts. As the oil is produced gas is loss so the oil loses some of the solvent ability and the fluid temperature begins declining as oil is produced out of the formation. Based on the amounts and types of paraffin present and an oil's ability as a solvent eventually the paraffin will start to come out of solution as a solid. The temperature at which this first starts to occur is called the Cloud Point (CP) or Wax Appearance Temperature (WAT). The longest chain n-alkanes are the first paraffin to come out of solution and will give an oil a WAT. As an oil is cooled below the WAT shorter chain n-alkanes will come out in greater quantity over an extended temperature reduction. In every oil there is much more Macro-crystalline paraffin ($C_{20}H_{42}$ to $C_{36}H_{74}$) than Micro-crystalline paraffin ($C_{37}H_{76}$ to $>C_{100}H_{102}$). This is why hard deposits (formation and lower tubing) are slower to build up but have a much higher melting point and surface deposits are softer and lower melting but build up much faster and in much greater quantity. If cooled to a low enough temperature the short chain paraffin will cause the oil to go solid 5ºF (3ºC) below the Pour Point (PP). It should be realized that as oil is produced from the formation to the stock tank that both the WAT and PP are changing as gas and paraffin come out of solution in the oil. The WAT and PP are lowest in formation oil (if bomb samples are retrieved and tested) and get higher in the tubing and higher in the flowline and higher in the separation equipment and are the highest in the stock tank. The highest paraffin content oil in any system is in the bottom of the stock tank and should not be used to hot oil wells.

It should also be realized that as the various chain length paraffin comes out of solution it gives up heat which means it will take much more heat to put them back in solution. This evolved heat can be measured by a calorimeter and has been used to determine the WAT of crude oils. A $C_{50}H_{102}$ paraffin crystal that comes out of an oil at a WAT of 100ºF (39ºC) will not melt back into the oil it came out of, in a short amount of time, unless it is heated to at least 180ºF (82ºC). This means that before running a cold finger test an oil should be heated to at least 180ºF (82ºC) for 1 hour to melt all of the longest chain paraffin back into solution to simulate the formation oil before it cools to the WAT or below. The difficulty of melting the microcrystalline paraffin back into solution has been understood for as long as the ASTM D97 pour point test has been run. According to this test to get a Maximum Pour Point for an oil you heat the oil to 115ºF (46ºC) at which temperature only the macro-crystalline paraffin is melted back into the oil giving the highest congealing point to the oil. To get the ASTM D97 minimum pour point you are told to heat the oil to 220ºF (107ºC) to make sure all the micro-crystalline paraffin is melted back into solution. The micro-crystalline paraffin is natural pour point reducers as the longest chain paraffin in an oil changes the crystal structure that forms. Oils with a large difference between the maximum and minimum pour points contain larger quantities of micro-crystalline paraffin.

## *SY*STEM TEMPERATURES AND HEAT TRANSFER

Every well produces an oil with a unique blend of solvents, paraffin and asphaltenes. This will give each oil in a field a different WAT, PP and color. Each well will start to get paraffin deposition at different depths or locations based on this variation in each oil. The type of production system will also affect where the paraffin starts to deposit. In a gas well in which all the fluids and gas are produced up the tubing you will have less cooling than in a pumping well with gas produced up the casing and fluid up the tubing. The gas in the casing cools the tubing and the rods create very turbulent production up the tubing in a pumping well. Turbulent production causes more rapid heat loss from produced fluids. Wells producing all oil and gas will have more paraffin deposition than similar wells producing a mixture of oil and water. Water will carry 2.8 times more heat than oil so wellhead temperatures tend to be warmer in wells producing water. These variations from well to well cause paraffin deposition to start at different locations from well to well in a field.

Paraffin starts to deposit when the **inner pipe wall** of the tubing, flowline or pipeline reaches the cloud point or wax appearance temperature of the oil in that well. The difference in temperature between the oil in the center of a line and the inner pipe wall is the driving force causing deposition. This difference in temperature between the oil and inner pipe wall varies from the bottom of the tubing to the surface vessels. The paraffin that is depositing on the inner pipe wall varies as the temperature changes from the formation to the surface vessels. When the inner pipe wall first reaches the CP or WAT the paraffin deposit will be only those paraffin that come out at that temperature which are the highest melting paraffin in an oil. These deposits will consist of the longest chain length paraffin in the oil. As the oil cools,, as it is produced up the tubing, shorter chain paraffin begins to come out of solution and the deposit has a lower melting point. This scenario continues with the temperature in the flowline getting cooler and the paraffin deposit getting a lower melting point because shorter chain length paraffin comes out of solution. If enough cooling occurs and the oil contains a high percent of macro-crystalline paraffin the oil may reach the oils pour point and congeal into a solid.

So the question becomes which paraffin do you want to inhibit in the system? The paraffin that deposits in the formation or tubing which has a very high melting point and is hardest to get to. The paraffin in the flowline which is lower melting and easier to get to? The congealed oil in the vessels or tank? If you are trying to stop deposition of paraffin in the formation or tubing you will need a test that reproduces that location in the well. You would want a test using a probe temperature no cooler than the wellhead temperature. As an example; if you have an oil with a CP of 120°F (49°C), a 10,000 foot deep well with a BHT of 140°F (60°C) and a WHT of 100°F (38°C) the paraffin would start to deposit ~5,000 feet from surface. In this case you would want a test to reproduce the paraffin that deposits between 120°F and 100°F in the tubing of this well. Using a cold finger test you would want the cold probe to be no cooler than 100°F (a warm finger) and the oil held at no more than 125°F.

In real production equipment the temperature difference between the oil and inner pipe wall surface is rarely more than 20°F difference. A real life example was a North Sea Platform which was started up with an empty pipeline, 20 km long and a 16 inch diameter. All oil leaving the platform was heated to 170°F (77°C) before being pumped into the insulated pipeline which was in 41°F (4°C) water. Initial production of oil was 2,000 barrels of oil per day. The oil arrived at the receiving platform at 19°C (66°F). At 20,000 barrels a day rate the oil arrived at the receiving platform at 11°C (52°F). This drop in temperature is caused by turbulence (turbulent flow), the higher flow rate mixes the oil so that the temperature drops more than in laminar flow. Heat transfer calculations on this pipeline system showed at most a 17°F (9°C) difference between the oil in the center of the pipe and the inner pipe wall temperature. This indicates that most systems will never have a great difference in temperature between oil temperature and inner pipe wall temperature.[5] If chillers are used to cool an oil, for stabilization purposes, then higher differences between oil and chilled surface may be encountered and the test should have a corresponding temperature difference.

## COLD FINGER TESTING

The Cold Finger test that is in widest use today consists of a heated bath to hold the oil at a higher temperature than the cold probes that are inserted into the oil in the hot bath. Commercially available Cold Finger equipment is available today that is very advanced from the first cold fingers developed back in the late 70’s and early 80’s. The first cold finger equipment that I observed was at a major oil company that had a one probe cold finger that required a lot of lab space. It consisted of a hot bath to hold the oil sample in a bottle with magnetic stirrer, a cold water bath, a circulating pump to pump cold water through the probe. Sample size was 400-600 ml of oil per run with run times varying from 6 to 16 hours.

Based on this oil company test equipment vendors started building similar equipment in many different forms. At the company I worked for we started with glass cold fingers, then mild steel probes and eventually ended up with stainless steel 1 inch diameter probes, 6 inches long which were immersed in 400-500 ml of oil in 600 ml beakers with magnetic stirrers in the bottom of the beakers. Tests were run overnight for 14 to 18 hours. The probes were immersed about 3 to 4 inches into the oil. Eventually 8 place equipment was built so that 7 chemicals or rates of chemical could be compared to one untreated oil sample called the blank. After a test the probes were drained while cold and then the paraffin was removed by scraping into a weighed aluminum dish. It was noted that at a higher probe temperature deposits were much harder, higher melting point, than deposits from tests with a colder probe temperature. In the early years of testing it was noted that reproducible results were hard to come by. We attempted to make sure the samples of oil were well mixed so all samples would be the same. Eventually we figured out that a sample of oil sent in to the lab had cooled to a low temperature and paraffin, both macro and micro, had separated from the crude. If we only heated the oil to reservoir temperature in an attempt to solubilize the paraffin back into solution we could not get reproducible results. It should be remembered that oil in a shallow formation has been held at that temperature for millions of years and it has never cooled below the CP or WAT. It was determined that to get all the paraffin back into solution in a short period of time we had to heat an oil sample to 180°F (82.2°C). This is like the pour point test, PPT, where you have to heat oil to two different temperatures; 115°F (43.4°C) for maximum pour point (because you only melt the low melting macro paraffin back into solution) or 220°F (104.5°C) for minimum pour point (because you have now melted most of the micro paraffin which changes crystal structure as it comes back out of solution). After heating a sample to 180°F (82.2°C) we would cool it to the temperature at which the chemical was to be added to the oil in the system. For downhole application this could be the reservoir temperature. The sample was now similar to the real oil in the formation that has never been cooled (all paraffin in solution). If we were working on a flowline problem where the chemical was added at the wellhead we could cool the oil to the wellhead temperature to add the chemical. Of course, the oil we heated has lost a lot of gas and is not like real formation oil which has a large volume of gas and has a lower CP or WAT. This means that the cold finger test is a more severe test because the oil has a higher percent paraffin and higher CP/WAT than actual formation oil. So if a chemical reduces deposition on the probes using this oil it should have a better chance of working on the oil in the well. So what we learned is that we need a large enough sample of oil that contains enough paraffin that we can weigh it if we run a deposit test at or near the CP/WAT. If you only use 100 ml of oil on a test the amount of micro wax that deposits may be to light to measure. If you have test results that say the CP/WAT of an oil is 140°F (60°C) then you should be able to get a deposit on your probe at 138°F (59°C) unless you have too little oil. Of course, if you use a 60°F (15.6°C) probe temperature while holding the oil at 120°F (49°C) on this oil you will get a very soft large deposit, that is unlike any you will get in the system. By using this large temperature difference it allows you to run a shorter test and get a bigger deposit on the probe. It is also showing that more chemicals have activity because the range of paraffin that is being deposited is very large from ~ $C_{24}H_{50}$ to $C_{70}H_{142}$. This distribution can be determined by using a High Temperature Gas Chromatograph (HTGC). In a good test you would like the paraffin deposited on the probe to be similar to a paraffin sample from the problem area in the system that you are trying to treat.

So a bad test is:

1) a large temperature difference between the oil and the probe,
2) a deposit that is not similar to that occurring in the system
3) a short duration test indicating a big temperature difference
4) a test not using system information to help determine what the probe temperature should be
5) a test using oil containing crystal modifiers already in the system
6) a test not using oil from the well with the problem trying to be solved
7) a test not heating the oil to 180°F or higher to solubilize paraffin that came out during shipping

A good test:

1) Uses a small temperature differential similar to system conditions
2) Uses a HTGC to get a deposit similar to system deposit that is to be inhibited, deposit from well
3) A longer duration test so smaller temperature differential can be used
4) Information gathered from the producer about the well, BHT, Depth of well, WHT, header temps
5) A oil sample from the well trying to be treated
6) A CP of the oil to determine where deposition starts
7) Crystal modifier free oil
8) Preheats oil to at least 180°F and then cool to test temperature needed

## CONCLUSIONS

Until a cold finger test procedure is standardized by an accredited testing organization such as ASTM or API we will rely on the chemical vendors to run the cold finger test.

If testing is required by an oil company to pick the best inhibitor for it's well. The oil company personnel should know enough to require the test be run in a scientific manner. They should also be willing to supply information and samples of the well to be treated. Information should include a well diagram, BHT, WHT, Header temperature, depth paraffin deposits in well if known, how the well will be monitored and preferences on how they want to treat the well. Treatments can include: squeeze treatments, treatments down the casing using a capillary line, treatments down the casing using overflush fluid, in small wells batch treatments that slowly feedback over weeks, or flowline treatments. Fluids needed may include chemical free oil, water and a sample of the paraffin to be treated.

Vendors should run tests that duplicate the fluids and conditions in the well where the problem is occurring. Vendors are also responsible for making sure oil and paraffin supplied by the oil company is taken in an acceptable manner insuring oil that represents the system fluid. If the oil is emulsified with water the test should be run with emulsified oil as long as it is stable at 180°F. The oil cloud point should be run to determine at what temperature paraffin comes out of solution. Before testing, oil should be heated to at least 180°F for one hour to make sure all the paraffin is dissolved back into solution in the oil to be tested. The oil should then be cooled to the system temperature at which the chemical will be added to the oil. If down hole then the chemical is added at formation temperature. If at wellhead then oil is cooled to the wellhead temperature. If into vessels or pipeline then the temperature of the system at the injection point. The cold finger equipment should be run with a 15-20°F temperature difference between the oil temp and cold finger temperature. This is much greater than the system temperatures will ever achieve. A HTGC or at least a melting point apparatus should be used to make sure the deposit on the cold finger is similar to the sample of paraffin supplied by the oil company from the area in the well to be treated. The paraffin should be removed from the cold finger in a manner that allows examination of the deposit. This means that using paper towels may not be a best practice as only a weight of deposit is gathered using this method. An untreated sample (blank) should always be run and this deposit is the one that should be tested for melting point or by HTGC. The % inhibition is the difference in weight between this blank and the chemical treated deposits. If the blank deposit is so soft it runs off the probe at the end of a test then you are seeing congealing oil not a paraffin deposit. Run the pour point test if the system deposits are similar this these soft deposits.

If everyone does what is required and this procedure is followed the chemical that is best on the test will work in the field.

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