Chemical Treatment Of Petroleum Emulsions

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When Colonel Drake drilled the first oil well in this country he was extremely fortunate in two ways; one, he discovered at a very shallow depth, as compared with present day footages; two, the oil he discovered was a paraffinic, golden colored crude which contained very few impurities. It was easily refined with simple equipment, and required no treatment in the field. The development of problems and their solutions, which are connected with the production of oil, have been gradual.

The wells which were drilled in Pennsylvania, West Virginia, and Ohio in the early days of the oil business were shallow wells, easily drilled, with low gas pressures, steady drive and relatively free of water. As oil production extended into the Southwest, problems multiplied. Spindletop, which came in in 1901, was drilled with the then new rotary rig. While producers were learning more about the technique of drilling wells, the producers were encountering new problems inherent to the industry. Different types of oils were produced. Wells were drilled deeper. Higher gas pressures were encountered, all of which complicated the problems of production and brought about particularly the problem of emulsified oil. In those instances where water or brine was produced along with such oils, accumulations of this emulsified oil or BS&W created an immense problem.

It is commmon knowledge today that when an oil well produces water, an emulsion of oil and water is formed. Normally, the water is in the form of small droplets within the oil phase. This emulsification may be caused by the action of the rods and pump, or by the action of the gas contained in the oil, or by any other mixing which brings the oil and water in intimate contact. Worm cups, pitted balls and seats, chokes, or any condition creating an orifice or causing a jetting action of the oil and water, is conducive to the formation of an emulsion.

At its best, it can be said this Basic Sediment and Water (BS&W) was a nuisance to the producers, but it was primarily a tremendous waste to the petroleum industry. Some of the produced water would settle out in a storage tank to be drained off after the application of heat. This, of course, dissipated the light ends. The refineries accepted the crude oil at that time with a much higher percentage of water than is permissible today. But still many thousands of barrels were burned or disposed of otherwise.

In the producing areas huge earthen tanks were constructed, many of these holding several hundred thousand barrels of this emulsified or "roily" oil. This oil, naturally, lost all of its volatile gases. It was exposed to rain, and the elements. Dirt blew in from the countryside and contaminated the oil. The heat of the sun and the effect of settling enabled the operators to skim off a few inches from the tops of these pits every day, but probably 75 percent - 80 percent of this oil was a total waste. The only way of disposing of the BS&W which accumulated was by setting fire to these pits, and burning as much oil as possible, and then running the residue into the creeks. This, of course, created a terrific problem of polution.

Such a situation prevailed in the Glenpool field near Tulsa when a young pharmacist from St. Louis was called in as a consultant on a gas explosion which had occurred in Oklahoma. This young scientist was William S. Barnickel, who availed himself of the opportunity of visiting the oil fields nearby. It seemed to him that something could and should be done about this tremendous waste which was occurring in the oil fields. He resolved to apply his skill to solving this problem.

Barnickel obtained samples of the emulsion from these pits, and tanks on the leases and carried them back to St. Louis where he experimented on them in his laboratory. He found that he could break the emulsion by the use of a metallic sulphate, in this case, ferric sulphate, and was granted a patent on this process. He agreed to treat this oil for a percentage of the money obtained from the sale of the treated oil with his iron sulphate method. Here again, the same god of fortune who had smiled on Colonel Drake also smiled on William Barnickel, because he was successful in this first endeavor to treat oil field emulsions. He made another contract to treat some of this waste oil in Louisiana, and was not so successful. However, the spark had been kindled and although he realized his ferric sulphate process was probably not the answer to all petroleum emulsion problems, he felt that he could find a better answer with further work and experimentation.

His next patent disclosed the use of a water softener. Ordinary soap is an example of this type compound. Barnickel experimented with many different kinds of soaps, some of these he purchased as soap flakes— other compounds he formulated and manufactured himself. This proved to be successful, although expensive by comparison with present day standard methods of breaking emulsions. This, you might say, was the birth of Tret-O-lite, and of the oil treating process. Encouraged by the success he had had and with more experimentation, a third patent was issued which is the outstanding invention in the field. This is called the "Modified Fatty Acid" patent.

While this method of treatment was extremely successful, a recovery of one thousand volumes of oil to one volume of demulsifier was considered satisfactory. Pipeline operators then were much more lenient than now, and most of the oil produced could be sold through the use of this process, and a great waste of a natural raw material was eliminated. Subsequent work by Mr. Barnickel and other chemists developed more efficient chemicals for use in demulsifying oils, and today, a ratio of 100,000 volumes to one volume of demulsifier is not unusual. Since pipeline specifications are much more strict today, than in those early days, this amount of demulsifier is required to do a much better job of cleaning up the oil.

Since that humble beginning in 1914, there have been over a thousand patents granted for processes and chemicals used in the treatment of emulsions.

Emulsion treating still requires a specific formula for the most efficient operation. Mr. Barnickel thought he could prepare a compound which would treat all types of emulsions. His dream was like the old alchemist who sought the philosopher's stone. Modern chemists, with their complicated research facilities of today, are still striving toward that goal. However, as with the philosopher's stone, it is doubtful that it will ever be achieved. Each emulsion must be tested and treated as an individual problem.

Perhaps at this time we should define an emulsion. The story is told concerning one of the great petroleum chemists, the late Dr. Gustave Egloff. On one occasion during a patent suit, he was asked by the questioning attorney, "What is an emulsion?" Dr. Egloff then spoke for twentyone days answering this question. I have no intention of going into such detail, in fact, I am not capable of doing so. First petroleum emulsions are of two types — oil-in-water, and water-in-oil. Most oil field emulsions are the water-in-oil type and we shall consider it mainly.

By definition, an emulsion is an apparently homogeneous mixture in which one liquid is dispersed as droplets throughout a second and immiscible liquid. In a water-in-oil emulsion, the oil is the continuous phase. Actually, the "water" of an emulsion need not be pure water, but may be brine or some other oil immiscible liquid. Likewise, the "oil" may be crude oil or other petroleum or vegetable oil.

To form an emulsion, water and oil must be intimately mixed in the presence of an emulsifying agent. This agent is usually surface active, at least in that it adsorbs at the interface. In a petroleum emulsion of the water-in-oil type, the emulsifying agent may be any number of things, insoluble oil-wetted sand, various minerals and salt, asphaltic or napthenic materials contained in the well fluids, etc.

If we mix distilled water and a refined mineral oil, such as kerosene in a test tube or bottle we can observe that the water and oil separate at once showing that a stable emulsion is not formed. However, by adding a small amount of an emulsifying agent, we find that on agitation the mixture becomes an emulsion and will not separate readily on standing.

(This will be demonstrated—distilled water and kerosene are agitated in a bottle or test tube and allowed to settle. Another bottle containing water and kerosene is agitated with a drop of asphalt and allowed to settle. The asphalt will act as the emulsifying agent.)

Since most crude oils do contain these emulsifying agents, or impurities, and since in the production of the wells, the water and oil are intimately mixed, due to the pumping or flowing action, or agitation through surface equipment, an emulsion is usually formed.

If we allow an emulsion formed in this manner to set for a time, we will usually see three easily definable layers in the system. At the bottom of the receptacle will be a layer of water which has settled out. Above that will be a closely packed layer of small water droplets and oil. Above that will be a small amount of fairly clean oil. Even such an incomplete separation requires an extremely long settling time, and if the clean oil layer were examined closely, we would find it still contains a small percentage of water and we might also find the water layer in the bottom of the vessel would contain small droplets of oil. A photomicrograph of an emulsion shows very plainly these minute droplets of water dispersed in the oil.

It was mentioned earlier that treating compounds are more or less specific and each oil must be tested and the proper chemical formulation must be determined before an efficient demulsification job can be done. This test work is usually done by your chemical service engineer. While the test method for selecting the proper chemical compound is no secret, it is highly desirable that an experienced man perform this work—one who is trained in the procedure and who is equipped with the various chemical formulas and laboratory equipment. Unlike other tests which are run on petroleum, such as BS&W content, gravity, viscosity, etc., this test is not an exact, scientific quantative determination. It is a mixture of art and science. It takes several months for a man to become a competent tester of petroleum emulsions. (The following will be omitted if time is short.)

Oil is tested in the field in the following manner:

A sample of the crude oil to be tested is poured into a number of prescription bottles, usually six or eight at a time. Usually 100 cc of the oil is poured into each bottle. The tester then adds a carefully measured amount of chemical in solution to the bottles. That is, one formula is added to one bottle and another formula to another bottle. These bottles are then agitated and allowed to settle with or without heat. After a certain amount of settling time, the amount of water which is collected in the bottom of the bottle is measured. The cleanliness of the oil is tested by centrifuge and the interface is tested to determine the amount of BS still remaining in the oil. This test is repeated a number of times until twenty, or thirty, perhaps more, chemicals have been tested. From the data obtained and by subsequent rechecks and varying of the procedure, a formula is chosen which is best suited to the emulsion being tested. An experienced operator can conduct this test and from it determine the approximate amount of chemical required, the approximate amount of settling time, the temperature required, the amount of agitation, and other factors required to produce the cleanest oil most effectively. I will not go into detail on this test because as mentioned previously, it is much easier and much safer to have an expert do this for you. I believe that most chemical companies offer this service free. Personally, I can speak for only one of them and I will state that we consider it part of our work to conduct this test on your lease, and we hold ourselves available at all times to do so.

(The following will be included if time allows.)

Field Treating Procedures

The equipment required for treating petroleum emulsions in the field is very simple. However, certain steps or processes are necessary for the resolution of any emulsion. The first step is the introduction of the correct chemical. This may be introduced in the flow line or down the well annulus, in the so called bottom-hole treating method, or, in the simplest form, tanks of wet oil may be treated by the introduction of chemical into the tanks with subsequent rolling and settling. The chief requirement is that the chemical be interspersed as well as possible throughout the emulsified oil. When we consider the high ratio of oil to chemical used in present day treating and that it is necessary for some of the chemical used in present day treating and that it is necessary for some of the chemical to come into contact with the film surrounding each drop of oil, it is readily apparent that a thorough mixing is absolutely necessary. For this reason, flow line mixing is usually recommended.

In this case, the chemical is pumped into the flow line at the well head during the time the well is produced. The pump may be actuated by electricity, gas pressure, or by the action of the walking beam, but it is essential that a small amount of chemical be injected continuously.

The second step of this sequence is obtained by chemical means, that is; controlled agitation. So our third requirement is coalescence. Coalescence is the gathering or accumulation of the water of the emulsion from relatively small droplets into larger droplets.

The fourth step in the treatment of oil is settling. Here the water in the system settles to the bottom of the tank due to the difference in specific gravity of the two fluids. In other words, the effect of gravity separates the heavier fluid from the lighter fluid.

I have purposefully refrained from discussing the mechanical methods of oil treating such as bun barrels, heater treaters, etc. The subject of this paper has been confined strictly to the chemical treatment of petroleum emulsions. Time does not permit a discussion of the recognized importance of methods other than chemical treatment.