Practical Chemistry of Oil Treating

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Chemicals have played an important part in the production of crude oil for many years. The present level of technical development makes it possible to have a wide selection of these chemicals to help solve some of the many problems encountered in this area.

One of the many problems encountered is the formation of emulsions of oil and water. These emulsions may be formed in many ways. For example, almost all crude oil is produced as an emulsion because of the presence of natural emulsifiers and particles in the crude, and the mixing of the oil and water as the crude is produced.

The present crude oil production in the United States is over 7 million BPD. About 50 per cent of this crude requires treatment to break the emulsion and reduce the BS&W (basic sediment and water) to less than .5 per cent. This treatment is necessary because pipeline companies and refiners will not accept oil with higher levels of BS&W since it increases the cost of transporting this oil and interferes with refinery operations.

The breaking or separation of these emulsions into clean oil and water may be accomplished in several ways; freezing or cooling, heating, the use of demulsifying chemicals, or any combination of these methods. Generally, in the oil industry, chemicals and heating are used. The chemicals used to break emulsions vary greatly in composition and are generally very complex organic materials. However, they have one common property: they are all surface active agents or surfactants -- the chemicals affect the surface properties of either one or both of the liquids in the emulsion.

The oil industry's development and use of these chemicals has grown steadily since the first crude oil was discovered by Colonel Drake.

Since then, as a result of continuing research and development, there is now a wide variety of special demulsifier formulations available to oil producers. These products can influence the degree of success or failure of equipment and represent a large investment in time and money. For example, to complete some of the more difficult wells today may require an expenditure of $500,000 to $1,000,000. Thus, misjudgment in the use and application of a chemical or technique can seriously affect the productivity of the well and the profit on this investment.

The present demulsifiers are generally described simply as "high molecular weight surface active agents." Actually, a typical formulation will consist of a mixture of active ingredients in a solvent such as heavy aromatic naphtha. The solvent is used because the active materials usually have a high viscosity and pour point and would be difficult to handle without some solvent in the formulation.

The mixture of active ingredients is usually used because some materials will give a fast initial breakout of the emulsion, but will not completely separate the oil and water; others will take longer to break the emulsion but will give a cleaner oil. Other ingredients may be used either to suspend or water wet particles such as paraffin, iron sulfide, etc.

There are many different compounds because there is a wide variation in both the amount and type of oil and the amount and type of water in the various emulsions to be treated.

Since the emulsions encountered vary widely, before a compound is selected for a new field or area, at-the-well testing is done. This testing is necessary both to select a chemical and to determine the most economical concentration to use. Requirements can vary from a few ounces to a gallon per 100 bbl of production; but usually one part to 15,000 parts production is satisfactory. Field testing is carried out in small glass prescription bottles; and a fresh sample of emulsion taken at the well head is used. Various chemicals and/or various concentrations of a particular chemical are then added to the emulsion. The bottles are shaken, then heated; and the breakout is observed. A centrifuge test can then be run on the better formulations to determine BS&W.

Many different methods and different designs for oil treating equipment have been found to be effective. The most common method provides for injection of the chemical into the flow line at the well head and insures good mixing and good dispersion of the chemical in the emulsion. The production is then sent to a heater-treater, then to a gun barrel or wash tank to separate the oil and water. After oil-water spearation the clean oil is held in stock tanks, then delivered into the pipeline.

The early production from wells such as Colonel Drake's came from a shallow depth and was an easily refined paraffinic crude. Gas pressures were low and the crudes were relatively free of water. About the only treatment consisted of pumping the crude into large pits. As the oil was dehydrated by settling, the top layer of clean oil was decanted and sold. But as drilling extended into this area, wells were deeper and gas pressures higher; and water and emulsions became a problem.

Crude oil emulsions consist of water in the form of small droplets dispersed in the oil. These droplets are small enough--about five millionths of an inch in diameter--so that they will not settle out. These droplets are also believed to be surrounded by a thin film which prevents them from combining into larger drops. These films may contain asphaltic material, sand, silt, paraffin, sulfides, and other organic compounds found in crude oil.

Demulsifying chemicals, as has been mentioned, are surface active materials which alter the surface properties of the oil and water so the droplets can coalesce and settle out.

These emulsions are formed as the crude oil and formation water are produced as a result of agitation or mixing and flow through small openings at high velocity. The flow through the small pores of the formation into the well bore with a drop in pressure and release of the gas dissolved in crude is one source of emulsions. On pumping wells, the pump itself can cause the emulsion. Other causes are flow through chokes, valves, and other restrictions.

Almost every type of chemical which has surface active properties has been tried as a demulsifier. Soaps and metallic sulfates were used at first; but great improvement was made when it was discovered that the water soluble sulfonates -- a by-product of refining lubricating oils -- were very effective demulsifiers and are still used today. Various sulfonates of other natural oils were then developed.

Recently, various synthetic organic chemicals have been developed. These consist of ethylene or propylene oxide combined with an alcohol, amine, phenol or a resinous material containing these groups. The water solubility can be varied by varying the ratio of ethylene or propylene oxide.

The selection of the best chemical for a given emulsion still requires field testing on the lease. Freshly produced emulsions tend to "set" soon after they are formed, and after an emulsion has "set" it will be more difficult to break and will require more chemical. This setting time can be very short -- as little as 15 min on heavy asphaltic oils such as Talco or as long as several hours.

The demulsifier formulation which is best for a given emulsion depends on two factors: the water and the crude.

The water can vary from very fresh to supersaturated brine solutions: the solubility of the demulsifier will vary with the salt content of the water. Since there is very little demulsifier relative to the amount of oil treated -- usually 1 to 15,000 -- it is important that this chemical is kept at the surface of the droplets. If the chemical is too soluble in water, all the demulsifier will be removed with these drops as the water is broken out. If it is not soluble enough it will not be able to break the emulsion.

The crude oil supplies the emulsifiers and affects the rate at which the water droplets will settle out as the demulsifier breaks the emulsion. The demulsifier will also have different solubilities in different crudes, and the crude will affect the ease of dispersion of the chemical in the crude. Low gravity, high viscosity crudes usually require more demulsifier than do high gravity crudes because of the inability to get good mixing of the chemical and the slow settling rate after the emulsion is broken.

While we may eventually know all about the chemistry of crude emulsions and how to break them, the final criterion for a demulsifier is, "How does it perform in the field?" A knowledge of how emulsions are formed and how they can be broken with chemicals is essential to get good performance from a chemical in the field.

Basically there are four operations involved in breaking an emulsion:

(1) Add the <u>right</u> amount of the <u>right</u> chemical to the emulsion.
(2) Disperse it.
(3) Allow the droplets to coalesce and;
(4) Allow them to settle out.

Since we have not as yet developed one chemical to treat all emulsions it is important to use the correct chemical and the correct amount for the emulsion. Too much chemical as well as too little chemical can be bad Some formulations will tend to emulsify crude and water if too much is added. Sometimes these chemicals will cause, after they have broken the normal emulsion produced, a reverse emulsion -- that is oil in water. It is also important to be sure that the chemical used has not been contaminated. In a sealed drum demulsifiers do not deteriorate; actually some improve with age. The active ingredient, however, is usually dissolved in a solvent and contamination with water or other materials can cause the high molecular weight chemical to come out of solution and settle out. Of course it is important to be sure that the chemical is actually getting into the emulsion: the chemical pump can be plugged.

But simply adding the chemical to the emulsion is not sufficient. The chemical must be dispersed throughout the emulsion so some of it reaches each droplet of water. The chemical should be added as soon as is possible after the point of formation of the emulsion. Injection at the well head is usually suitable.

Even though the chemical has been dispersed throughout the emulsion, the emulsion will not break instantaneously and separate into oil and water layers. A long period of coalescing and settling may be necessary. Coalescing time is necessary to allow the small droplets to combine into drops large enough to settle out. And in very low gravity, high viscosity crudes may require long settling periods

Even after emulsions have been broken they can be reformed by agitation. In fact, usually these emulsions will break out easily by themselves after agitation is stopped. Any mixing or agitation will, however, slow down the separation process.

Future developments in demulsifiers will be in the area of wider versatility. Any one of the demulsifiers available today will usually do some good on a great variety of emulsions. However, there is usually one best and most economical chemical for any specific emulstion; therefore manufacturers of demulsifiers have such a large number of formulations available. In the future, there will probably be much more versatile chemicals; and, where 30 or 40 different chemicals are offered today, only four or five may be needed tomorrow