The Use of Chemicals to Break Oil Field Emulsions

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INTRODUCTION

Since the early days of oil production, operators have been plagued by emulsified oil. It has been estimated that about 70 per cent of all crude oil is produced in the emulsified form. Before this oil can be transported and refined the emulsified water must be removed. In the early days of the industry, pipe lines would accept oil containing upwards of 5 per cent water, while today they will accept only 1 per cent water of basic sediment.

Many methods of removing the water and emulsion from this production have been tried with varying degrees of success. In the early days of flush production the "cut oil" or "roily oil" was flowed or pumped into large earthen pits where it was subjected to treatment by the sun. This slow process produced a top layer of dry or "clean" oil which was decanted periodically and sold. Most of the light fractions were lost in the process but little thought was given to the loss as kerosene was the more important fraction and oil was being produced as fast as it could be dehydrated and sold.

Later, some improvements were made by the use of hay tank filters. Centrifuges were tried at some refineries and electrical demulsification was used in the oil fields as well as in refineries. When the operators discovered that lye, washing soda, and strong soap powders such as the old "Gold Dust" rosin soap would break these emulsions, the use of chemicals in oil fields began.

NATURE OF CHEMICALS USED

Most crude oil emulsions are emulsions of water-in-oil. The water is dispersed in very small droplets in the oil. Each droplet is surrounded with a thin emulsifying film which is believed to contain asphaltenes, sand, silt, paraffin and high molecular weight nitrogen materials found in the crude.

As in all emulsions, this film prevents the droplets from joining or coalescing to break the emulsion. Demulsifying chemicals can be described as surface active materials which, when mixed with the oil, will have a great enough affinity for water to break the emulsifying film and allow the water to fall out of the emulsion.

Almost every group of organic chemicals exhibiting surface active or wetting properties has been tried in laboratories or used commercially to break crude oil emulsions. Shortly after the use of soaps and salts gained prominence in the oil fields, the sulphuric acid derivatives of hydrocarbons were introduced. Great improvements were made when it was discovered that the water soluble sulphonates resulting from the refining of lubricating oils with sulphuric acid were good demulsifiers. These materials are still being used in quantities to treat stored tank bottom emulsions.

Sulfated oils were then found to be equally effective and in many places more effective than the petroleum sulphonates. These products were made by treating a fatty oil such as castor oil, corn oil, palm oil or fish oil with sulphuric acid. Like the petroleum sulphonates they were used in the field either in the raw acid form or neutralized with ammonia, sodium hydroxide or an amine. These sulphuric acid derivatives were very popular in most of the demulsifier formulations until about the end of World War II.

Further Progress

Along with the use of sulphuric acid derived demulsifiers, many other synthetic materials were used such as blown or oxidized fatty oils, sulfurized oils and alkylated naphthalene sulfonates. Further progress in providing better demulsifiers was made by the use of esterified derivatives of vegetable oils and organic acids. As petro chemistry grew and ethylene derivatives such as ethylene glycol and polyglycols became available, these products were used in the esters in place of glycerine.

These esters were the early non-ionic demulsifiers and their surface active properties were contributed by the ether linkage of the polyglycols instead of the sulphuric acid or organic acid groups. They were more effective than the old products; part of the effectiveness can be attributed to the fact that they were less susceptible to the hardness of the emulsified water and part to the fact that larger molecules could be built.

Present day crude oil demulsifiers are based on the ether linkage such as found in the polyglycols. Ethylene oxide and propylene oxide from our petrochemical plants are reacted on some starting material such as an alcohol, phenol, amine or a resinous material containing these groups. Each product is specifically made for emulsion breaking and they vary primarily in their affinity for water. High ratios of ethylene oxide are used to make water soluble chemicals for high salt content waters. In contrast, high ratios of propylene oxide to ethylene oxide are used to make demulsifiers for emulsions containing very fresh water.

SELECTION OF CHEMICALS

While the manufacturing of chemicals to break crude oil emulsion can be considered scientific, the selection of the most efficient chemical to treat a particular emulsion is still a "cut and try" method. Chemical companies find it necessary to conduct their screening of demulsifier materials on fresh emulsion on the lease. Emulsions, as we know them, are produced by the shearing forces of the choke, gas lift or pump and they are formed as the oil is produced.

As soon as the emulsion is produced the emulsifying film begins to "set" or orient itself by the leaching action of the water on one side and the oil on the other. This setting period varies with the oils produced and it may be as short as fifteen minutes on heavy asphaltic oils such as Talco or several hours on Gulf Coast emulsions. After the emulsion is "set" it does not respond readily to the small quantities of demulsifier normally used to give a complete break.

Larger quantities of chemicals will break the emulsion, but different chemicals tend to give the same treatment thus losing their individual characteristics. The chemical salesman does his testing on the lease with fresh emulsion. All companies selling demulsifiers equip their men with miniature laboratories either in a sedan or station wagon so that he can select the most efficient demulsifier for each field.

Crude oil emulsions have two important variables — the emulsified water and the oil. In general, we find that the method of producing the emulsion has little influence on the selection of a chemical. It is true that the replacement of a worn pump or the change of a choke size will change the degree of emulsion and its stability, but it does not produce a demand for a different chemical.

Probably the most important factor in the selection of a demulsifier is the nature of the emulsified salt water. Emulsified water varies from very fresh water to super-saturated brine solutions. If we visualize the ideal demulsifier, so well balanced that it has just enough affinity for the water to break the emulsifying film and not enough solubility to be lost in the separated water, we can readily see our problem. Theoretically we can never obtain the universal demulsifier for all emulsions.

If the chemical is too soluble in the water, we lose it in the first water droplets broken out. If it is not soluble enough it is carried through with the oil and B.S. is usually left in treated oil. The properly balanced demulsifier can be described as not quite soluble in water and not quite soluble in oil. When such conditions exist we believe the emulsifier is bouncing from one emulsified droplet to the next, so that each molecule is "worked" several times before the emulsion is completely broken.

Actually, the chemical is not in solution but is in a suspension as a colloidal material. At the low concentrations of one part of chemical to some 10,000 to 40,000 parts of emulsion, measurements of solubility are difficult. For practical purposes we inaccurately describe the product as oil soluble or water soluble.

Different Chemicals Needed

Crude oil, the other important variable, contributes the emulsifying film and the problems of treating the many emulsions. Crude from each geological formation produces an emulsion which is different from other formations. The differences are noted in the speed with which the emulsion is broken, the amount and severity of interface emulsion, the rate of settling and the chemical used. These differences can be attributed to the gravity of the crude and its solvency.

Low gravity and high viscosity crudes, especially the heavy asphaltic types, generally require more demulsifier than high gravity coastal crudes. Poor dispersion or mixing to get the chemical to each emulsified droplet may account for part of the problem. Slow settling rates are improved by filter beds such as hay tanks.

The solvency characteristics of a crude, when measured by the aniline point or Kauri-Butanol value, have been studied. Such data, correlated with the solids content of the water, are useful on a research basis to explain why similar crudes may require different chemicals. Final and useful results are still obtained by actually bottle testing the demulsifier in the field.

Frequently people ask why so many demulsifier formulations are made and if they are really necessary. Modern demulsifiers are a great improvement over those of ten to twenty years ago. Instead of three or four old chemicals for each field, we now find most fields with only one chemical. This reduction in the number of chemicals has come about by the development of chemicals which work well on a wider range of waters and crudes.

The use of several chemicals in one field was common because the water varied from one end of the field to the other. By properly balancing the older chemicals and using about three chemicals to a field, chemical companies could offer a real saving to the producer.

Today, one chemical is able to treat the whole field with only a token loss in efficiency. The difference in chemical demand from one end of the field to the other is usually less than the amount of chemical used as an insurance factor by the pumper or switcher. This extra amount of chemical, over the very minimum needed, takes care of variations in production and costs very little.

Fewer formulations of demulsifiers could be made but some efficiency would be lost. The active competition existing in the chemical demulsifier field precludes any compromise in efficiency. New and improved formulations can be expected as long as we have emulsions to treat.

FIELD PROBLEMS IN THE APPLICATION OF CHEMICALS

When treating troubles occur on the lease, the chemical salesman is usually available to help out within a few hours. As he is familiar with his chemical, the lease, and many other oil fields, he can render a needed service. Most of his trouble calls turn out to be something other than chemical.

He knows that the chemical in the drum does not change from good to bad overnight. Demulsifier chemicals have a storage life as long as the steel drum. Sometimes they even appear to improve with age. In his investigations of the trouble, he may search for answers to the following questions.

1. Has the drum of chemical been contaminated with rain water and caused a stratification?
2. Is enough chemical being used?
3. Is too much chemical being used? (This is unusual with modern chemicals except when several people try to treat out a tank and each uses additional chemical without telling the other.)
4. Has a well producing pipe line oil to storage started making water?
5. Have tank bottoms been circulated through the system without the use of additional chemical?
6. Is the syphon leg stopped with scale or shut off forcing B.S.& W over into the stock tank? Is the water level too high or too low?
7. Is the heater treater or gun barrel part full of sand?
8. Is the oil and gas separator leaking gas to cause the heater or gun barrel to roll the emulsion?
9. Is the chemical pump stopping at night due to a drop in gas pressure or freezing up?
10. Is the underground line from the chemical pump to the flow line broken? When this happens the chemical is usually not visible on the surface.
11. When was the relief man on? Relief men are not as familiar with a particular lease as the regular pumper.
12. Is the chemical the wrong one? He may be using the wrong chemical or the emulsion has changed. Emulsions do change due to changes in the brine content of the produced water. The change is slow but progressive. The time for a new chemical arrives.