Use of Chemical for Breaking Emulsions

By B. M. McCASKILL, Jr.
Visco Products Company
Hobbs, New Mexico

In the early stages of the production of oil in the Pennsylvania and West Virginia fields, very little, if any, "bad oil" or emulsions were found. The small amount that was made created a very minor problem. The reason for this small amount of emulsion was due to the fact that oil produced in those fields was almost void of any foreign matter. Also, what water was produced was almost pure and very little gas was found. This kind of condition will not make an emulsion. This will be explained later.

As the production of oil moved into the mid-continent area, more and more emulsions, commonly referred to as B S & W, were found. B S & W is merely the short name for basic sediment and water. About this time, it was believed, and still is, that oil originated from animal and plant life that was buried far beneath the surface during earlier geological periods. This animal and plant life that was buried beneath the earth began to decay, creating gases, and built up tremendous pressure. Lying in this state for untold millions of years, oil deposits were created.

When the producers first began to see this discolored oil, which we know today as emulsion, many of them were of the opinion that it was oil that had been brought to the surface before it had time fully to mature. That is why the term "green oil" or "bad oil" was coined. This mass was usually drained off into large sumps or pits, and was either covered by dirt, or allowed to overflow into the streams and ditches. However, many times before it was disposed of, it was noticed that a certain amount of the oil would rise and the pit would act as a "treating plant". Production men realized that more of the clean oil would separate if they could help nature by creating artificial heat. Consequently, steam coils were placed in the pit and rows of steam boilers were installed to supply them. This was a crude and expensive method of treating oil, and many times it was impossible to reclaim more than half the oil actually produced.

Soon oil had become a very necessary part of the American way of life. Big corporations and companies had been formed to produce oil. As the production increased, the emulsion problem increased. The companies, realizing that some better way of separating the water and oil had to be devised, installed large tanks, both wooden and steel, placing steam coils inside them. This method proved superior to the old pit system, however, it was far from perfect. Not only did the emulsion that was not treated create a disposal problem, but much of it was impossible to break down with the heat alone, consequently other methods were sought.

The first commercial treating chemical was a solution of a cheap soap chemically equivalent to Gold Dust Cleaner, a product familiar to our grandmothers. It is believed that a switcher cleaning his hands with this Gold Dust Cleanser noticed that the emulsion turned from brown to black and the water separated. From this basic idea, chemists investigated most of the soap-forming materials running from the simple fatty acids to the complex acids derivable from animal, vegetable or mineral oils. Simultaneously, most of the known saponification reagents were used to prepare the less common soaps of these fatty bodies. As a group, the soaps had one common disadvantage and that was their water softening action to yield insoluble soap that frequently stabilized emulsion.

The next step chemists took was the use of castor oil and sulphuric acid, they noted by adding alkyl groups to the molecules demulsifying action appeared.

Not many years ago it was the considered opinion of several experts in our industry that no efficient demulsifier could be developed without using castor oil as a basic raw-material. Wartime shortages of castor oil and intensive research have confounded the experts, for today castor oil-derived compounds are by far in the minority. Today we know that a successful emulsion breaking chemical is an oil soluble molecule to which water soluble groups are added until the desired balance has been attained. This knowledge has been acquired slowly over the years in the evolution of treating chemicals from the early use of caustic soda to today's modern efficient and economical chemicals.

Mechanical and petroleum engineers were also constantly at work on better treating plants. As oil became more valuable, more effort was put forth to reclaim as much of the oil as possible. From this beginning was developed the modern treating plants and emulsion breaking compounds that we have today.

At this time we will try to think about the thing that has cost, and is still costing, the oil companies many millions of dollars annually. What is an emulsion? The answer is simple -- an emulsion is a mixture of two immiscible liquids, one dispersed as globules in the other. In our case, it is a water and oil emulsion. At least three conditions are required to make an emulsion. Besides the immiscible liquids, there must be an emulsifying agent and agitation. There have been many theories expounded as to what the emulsifying agent is that creates oil field emulsion. We think of dissolved salts, paraffinic bodies, asphalt particles, sand, lime, scale and others. In any case, we know that we do have emulsions. Whether or not emulsions are made in the bottom of the oil well is a matter of conjecture. We do know that many of them are formed coming through leaking pumps and small chokes.

We, in the manufacture of emulsion-breaking compounds, consider that emulsions are the source of our bread and butter. But, how many of us realize that we probably would not exist if we had not had available at birth an emulsion, for milk is an emulsion. And as we grew older we considered emulsions as one of the necessities of life, for who would like his bread without his butter? and butter is an emulsion; in fact, it is the very type of an emulsion with which we are now concerned, an oil and water emulsion. Ninety-eight percent of the emulsions found in the oil fields are of this type.

To know much about emulsions, we must first think a little about the laws of nature. It is known that all masses are built of molecules, whether or not they be solids or liquids. These molecules are in a constant random motion. The rapidity of this motion is governed by the temperature. In the case of this motion in liquids, it is called Brownian movement.

In thinking about two immiscible liquids, which means two liquids that will not mix into a true solution, let us stop here and talk a little about solutions. There are two different kinds of solutions, one known as a true solution, the other a disperse solution. For example, salt and water, and sugar and water make true solutions, oil and water or sand and water make dispersed solutions. Ink is a dispersed solution. The resulting colors of these dispersed solutions are caused by a diffusion of light. Many times a good treating engineer can determine close to the amount of water being produced by looking at the color of emulsion. However, we would not suggest this method if a centrifuge machine is available.

Now that we have given the definition of an emulsion, we must determine how emulsions are formed. When two immiscible liquids (oil and water in this case) are forced through a small opening, the water is broken into minute particles, frequently so small they can only be seen through a microscope. When these fine droplets are scattered through the oil, they make a dispersed solution. If these droplets are broken into microscopic size, the force of gravity will exert less effort than the constant random motion of the Brownian movement and a stable solution results. An example would be homogenized milk. If this were the only thing that happened, eventually enough of these microscopic particles of water would coalesce, forming a drop large enough that the force of gravity would overcome the Brownian movement and it would settle. But for us to see further into the formation of emulsions we must study nature a little more.

A drop of water in suspension is a perfect sphere; it is not flat, square or oblong. In fact, all bodies of liquid have a tendency to be globular, and would be a perfect sphere if they were not distorted by the force of gravity. It becomes globular because this is the smallest amount of surface for any given mass. If we can imagine a molecule that has wandered to the surface joined on each side and underneath by the other molecules having a drawing effect toward the center with practically no exertion from the outside, we can understand that a liquid being pliable would have a tendency to become globular. This action can be likened to the force of gravity of the earth. This pulling force forms what is known as surface tension. This force, with the help of the emulsifying agent, forms a film around each minute droplet of water isolating it from other droplets of water, which have films formed around each one of them. This makes it impossible for them to ever come together and form a larger droplet. Here we have an emulsion. The dispersed solution becomes much more stable due to this mixture making a viscous mass. The viscosity of an emulsion in most cases is more than the fluids that comprise it. The entire formation of an emulsion takes place in a small part of a second.

Now that we have determined what an emulsion is and how it is formed, let us go into the study of how to break it. As we have said before, much study and many experiments have been run as to the most efficient way to cope with the emulsion problem. It was found early in the process of treating oil and water emulsions that the most efficient way to break down an emulsion was the combination of an emulsion-breaking chemical and the application of heat. Many types of chemicals have been produced. It has been found that no one chemical or combination of chemicals could be compounded that would be suitable to all types of emulsion. Therefore, it has been necessary to manufacture many formulas to cope with the emulsion problem. There are several efficient compounds now on the market; in fact there is an efficient formula for almost any type emulsion.

These new type compounds are much nicer and cleaner to handle and pump than our old type compounds which were sticky, tenacious material which almost defied removal from hands, tools and clothing.

Today field men are trying to educate the oil industry in using these new compounds to get the most efficient results. Because of the much faster action of these compounds you can use too much chemical, as well as heat, thus building high bottoms in the storage tanks which will have to be circulated plus the use of a neutralizing compound. This not only costs the company extra chemical but the loss of gravity. I find in cases where you have a high paraffin base oil, which is mostly what we are dealing with in West Texas and New Mexico, if we use too much chemical and heat we not only suspend some of the water up in the oil but it will make all the paraffin congeal and fall to the bottom. That is why it is very important to get your emulsion checked by an experienced treating engineer so he can run you a bottle test with different compounds and at different ratios of chemical plus different temperatures. He can then give you the chemical that is best suited for your emulsion plus telling you what temperature to carry on your treating plant and also where to set your chemical injector to give you the best treating possible.

I find the most difficult emulsion to treat is one that has a high precentage of paraffin and iron sulphide. This combination will build up in the treating plant and carry water with it over into the stock tanks which results in a high bottom. Often times you try to circulate this type bottom with no avail. The best way I have found to cope with this condition is to use a good paraffin chemical while circulating. This will tend to put the paraffin crystals back into solution with the oil, and release the iron sulphide and water to go to the pit. The water will be a blackish color after using this type chemical.

Some oil companies are trying to treat their emulsions cold with a good fast acting chemical plus a large settling tank with automatic water removal. This method might be nearer than we think because it is being done in lots of areas. This method has advantages in that you get a better gravity of oil, and less corrosion and scaling; consequently, the upkeep on their treating plant is lower. They have no fire tubes to replace and it is a fact that heat aggravates corrosion and scale wherever it is prevalent; however, it is difficult in the winter months to treat a stable emulsion with a small percent of water without some heat. After the wells get older and start making more water, usually more foreign material is in the oil; they begin to have Heater treater trouble, such as sulphide corrosion and calcium carbonate scaling which either eats holes or plugs up the treaters. Some companies have started eliminating heat and treating cold successfully in these type wells which we call strippers.

In trying to give in detail the reaction of emulsion to heat, and the part that treating compounds play in the process of oil treating, we will begin by comparing each droplet to the different sizes of eggs. In the case of an egg, the thickness of the shell depends on the size of an egg. For example, a goose egg has a much thicker shell than a humming bird egg. We also have different sizes of droplets in the same emulsion, but different from the egg, the film is of the same thickness regardless of its size. However, in a different gravity of oil, there would be a film of a different thickness and possibly a different type. This is the reason why different emulsions require different treating compounds and varied temperatures. It can be understood that the larger droplets of water in an emulsion would be much easier broken than a small one for the simple reason that the film on each is the same. As a comparison, if the shell on a humming bird egg were as thick as that on a goose egg, the humming bird egg would be much more difficult to break. Due to this situation, we find that perhaps emulsions having only a small percentage of water would be much more difficult to separate than others with a greater amount. This is a constant source of misunderstanding among field men. Many of them think that because they are making one or two percent emulsified oil, it should not be difficult to break. There is another factor that enters into this problem. The smaller the droplets, the greater amount of time is necessary to form a droplet large enough for the force of gravity to overcome the Brownian movement.

It is believed that when the treating compound is mixed with the oil, it attacks the film. Some chemists believe that a form of electrical shock is thrown off and gives the globule of emulsion a slight twist, disrupting the film and releasing the water. Another theory is that the acid neutralizes the film, allowing the droplet of water to escape from its prison. We know in most cases this happens -- that it is necessary to heat the emulsion, and we are of the opinion that the heat either weakens or softens the film, allowing the treating compound to get directly to the water and break the surface tension. The heat makes the emulsion thinner, and the chemical less viscous, thereby making them much easier to mix thoroughly, which is an absolute necessity in the process of breaking an oil and water emulsion.

Up to a few years ago, the producers of oil spent very little time worrying about cost in the process of treating oil. First, as a rule, there was plenty of fuel gas which had little, if any, market value. Also, most oils were not sold on a gravity basis; consequently, the main object was to get the oil out of the ground and get it ready for the pipe line. Today we have a very different situation. The wet gas produced with the oil has become very valuable. Gasoline plants have been erected in most of the oil producing areas and premiums are paid for gas. And it is known that a part of our petroleum chemicals are obtained from the lighter ends that have previously been evaporated through the process of heat treating emulsion.

Most of the companies, realizing the tremendous losses that are occurring with obsolete treating methods, are constantly trying to find more efficient methods of dehydrating oils. It is known that for each degree of gravity oil is lowered, at least 2 percent in volume is lost. We are sure this is a very conservative estimate, and in many cases, the loss is much greater. Engineering departments are busy experimenting with varied methods of heat treating emulsions. Chemists are constantly at work trying to find treating compounds that will react at lower temperature. Consequently, more efficient methods of oil treating are being devised.

Not only is the conservation of oil being given much study, but another problem in the process of heat treating is a constant source of trouble. This is corrosion. Salt, lime, sulphur and other foreign matters found in the water, oil, and gases create a major problem. In many instances, when this type of emulsion is heated, these chemical elements are converted into acids that are very damaging to equipment. The higher the temperature the more they react; thereby making it necessary, not only from a conservation standpoint, but for corrosion as well, to dehydrate oil with the lowest possible temperature.