Proper Use of Chemicals for Breaking Emulsions

By B. M. McCaskill, Jr.

Visco Products Company
Hobbs, N. M.

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 these 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 was merely the short name for basic sediment and water. Even today the term B S & W is standard for emulsion. About this time, it was believed, and still is, that oil originates 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 gasses, 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 this was oil that had been brought to the surface before it had time to fully 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 to the surface, after nature, with its sun and wind, 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 of the oil actually produced.

By this time 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 over the old pit system; however, it was far from being 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 marine, 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 our 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. Taking the place of castor oil is a class of compounds which permit practically a tailor-made composition of any design or characteristic. Since most of this work is currently in progress, we are not at liberty to disclose any of the details. I have worked in fields that the treating cost averaged about 12 cents per barrel using our castor oil base compounds, but today in the same field this new type compound is doing the same job for mills per barrel. This has happened in the short time of 5 years. Our chemists have worked hard to make these compounds for the oil industry possible.

Mechanical and petroleum engineers, also were 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 two immiscible liquids, one dispersed as globules in the other. In our case, it is a water and oil emulsion. At least three different things are required to make an emulsion. Besides the two immiscible liquids, there must be an emulsifying agent. There have been many theories expounded as to what the emulsifying agent is that creates oil field emulsions. We think 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 encountered an emulsion on our birth, as 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 is 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 zig-zag motion. The rapidity of this motion is governed by the temperature. In the case of this motion in liquids, it is called the Brownian movement. We shall refer to this motion from now on in this discourse as the Brownian movement.

In thinking about two immiscible liquids, which actually 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 fusion 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 by pressure, the water is broken into minute particles, many times so small they can only be seen through the lens of 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 zig-zag motion of the Brownian movement creating a stable solution. An example would be homoginized milk. If this were the only thing that happened, eventually enough of these miscroscopic parts 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 a little more about nature.

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 or terrain of the earth. 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 fluid that retains it. The entire formation of an emulsion takes place in a small part of a second, probably with an action faster than sound, or as fast as electric current. There have been some theories that it is some form of atomic energy.

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 emulsion 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 formulated 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. However, as it is necessary in conjuction with treating compound to apply heat, many types of heaters have been manufactured.

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

Today we field men are trying to educate the oil industry in using these new compounds to get the most efficient results because due to 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.

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 bird egg. We also have different sizes of droplets in the same emulsion, but different to 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 element. This is the reason that different emulsions require different treating compounds and varied temperature. 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 bird egg were as thick as a goose egg, the bird egg would be much more difficult to break. Due to this existing situation, we find this in oil treating—that perhaps oil that only has a small percentage of water, would be much more difficult to separate than another with a greater amount. This is a constant source of misunderstanding among many 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, eruping 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 melts or softens the film, allowing the treating compound to get direct 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 thoroughly mix, which is an absolute necessity in the process of breaking an oil and water emulsion.

Up to a few years past, 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 gas for fuel 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 a proven fact that for each degree of gravity oil is lowered, at least 2 percent in volume is lost. This conclusion was established by the engineering department of one of our leading universities of the South. 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 working trying to find treating compounds that will react with less 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 gasses are creating a major problem. In many instances, when this type of emulsion is heated, these chemical elements are converted into acids that are very severe on equipment and destroy them in short periods of operation. 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 least possible amount of temperature.

As we review the history of the production of oil and the process of demulsifying it, we see that this is merely another battle between Mother Nature and mankind. He, trying to obtain from her the necessities and luxuries of life; she, trying to retain her own.

His purpose, to build a better way of living; hers to prorate her substance to him. This contest has been going on since the beginning of man's creation and will continue throughout the centuries to come.

☆