Application of Surfactants in the Petroleum Industry

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ABSTRACT

Surfactants are used throughout the petroleum industry. Some of those uses are mentioned in this paper. Market growth in surfactants for refinery products probably will be small. More rapid growth is anticipated for surfactants used in the oil field. A large potential market exists for surfactants in enhanced oil recovery, but many technical and economic problems remain to be solved. However, it would seem, as we enter the last decades of the "petroleum age," that enough of those technical problems will be solved and that the oil we leave behind will become valuable enough to allow some methods of enhanced oil recovery to become economical, commercial processes.

INTRODUCTION

Say "application of surfactants in the petroleum industry" to a refinery person, and he may think of gasoline, lubricating oils, or asphalt emulsions; say it to an oil production person, and he may think of drilling muds, demulsifiers or enhanced oil recovery. The fact is, surfactants are used throughout the petroleum industry.

In some petroleum applications, surfactants perform in their more conventional role—as detergents or dispersants. In other petroleum applications, surfactants play more unusual roles. The intent of this paper is to discuss briefly some of the many applications of surfactants in the petroleum industry and show for each application what the surfactant does and what chemical types of surfactants are most commonly used.

This paper does not describe a market survey. No volume figures are given. Many of the statements concerning potential growth have not been submitted to experts for confirmation. The aim is to familiarize the reader with some of the applications of surfactants in the petroleum industry.

Since it is relatively new and the potential volume is large, applications of surfactants in enhanced oil recovery are emphasized.

Gasoline

Surfactants are added to gasoline as detergents, dispersants, corrosion inhibitors and carburetor anti-icing additives. The detergents are designed specifically to reduce deposits in the throttle section of the carburetor. The dispersants reduce deposits not only in the carburetor but also at the intake ports and on the intake valves. A good dispersant also will extend the life of the PCV valve. The more general term "deposit control additives" encompasses the functions of gasoline detergents and gasoline dispersants and also includes additives which reduce varnish and sludge deposits in the piston and rocker arm areas. Ignition control systems, such as positive crank case ventilation and exhaust gas recirculation, increase the likelihood of harmful deposits and increase, thereby, the need for effective surfactants for gasoline.

Most gasoline additives burn without leaving residual ash. Nonionic deposit control additives include long-chain alkyldiamines, alkylsuccinimides of diethylenetriamine, alkylphenolic amines, and alkylimidazolines. Ionic deposit control additives include amine salts of alkylcarboxylic, sulfonic and phosphoric acids. Amino and amino-amido derivatives of low-molecular-weight (MW) hydrocarbon polymers also are used as deposit control additives.

Surface-active corrosion inhibitors tend to be ashless anionics such as alkylcarboxylic acids and amine salts of alkylcarboxylic, sulfonic and phosphoric acids. The amine salts of alkylcarboxylic, sulfonic and phosphoric acids are used also as carburetor anti-icing additives as are ethylene oxide derivatives of alkyl imidazolines and alkylamides.

Due to longer oil drain periods and engine deposits caused by air pollution devices, the market for gasoline additives has grown faster than the market for gasoline in recent years. In the future, however, the two markets should grow at more similar rates; and with slow growth, at best, projected for gasoline volume, the growth of the gasoline additive market should be similarly slow.

Diesel Fuel

Detergents, dispersants and corrosion inhibitors, similar to those used in gasoline, are being used in some diesel fuels. Deposit problems which occur in the carburetor in gasoline engines are transferred to the fuel filters and injectors in diesel engines. Use of diesel engines in passenger cars is becoming more popular. To the extent that diesel engines simply replace gasoline engines and the additives are the same, no net change in the additive market occurs. However, additives designed specifically for diesel fuels may be a new and growing market.

Jet Fuel

The same surface-active corrosion inhibitors used in gasoline and diesel fuel are added also to jet fuel. In addition, some jet fuels contain antistatic additives which reduce the chance of sparking caused by static electricity generated during flow. Manganese alkylsuccinates, chromium alkylsalicylate, alkylamine salts, monocarboxylic and polycarboxylic acids, and amine derivatives of maleic anhydride copolymers are used as antistatic agents. The market for jet fuel additives should follow the same modest growth as the market for jet fuel itself.

Engine Oils

In engine oils, as in fuels, surfactants are used largely as detergents, dispersants, and antirust agents. However, the mechanisms are quite different in oil than in gasoline. Both ash-producing and ashless surfactants are used in lubricating oils. Some surfactants retard carbon and lacquer deposition by adsorbing on engine surfaces; some form micelles in the oil in which deposit-forming impurities can be sequestered. Also, detergents are used frequently to suspend inorganic alkalinity, such as calcium or magnesium carbonate, in the oil. Such alkalinity reduces corrosion by neutralizing acidic combustion products from the fuel and oxidation products from the oil.

Chemically, the ash-producing engine oil detergents are petroleum sulfonates from lube-oil-range aromatics, alkylbenzene sulfonates, petroleum naphthenates, alkylphenates and alkylsalicylates—largely as the barium, calcium or magnesium salts. Alkylsuccinimides and pentaeyrithritol hydroxyesters of succinimides are examples of ashless engine oil surfactants.

High-MW, ashless, polymeric dispersants play a dual role in engine oil. In addition to keeping deposit-forming materials suspended in the oil, they improve the viscosity/temperature characteristics of the oil. Methacrylate copolymers in which the comonomer is vinylpyridine, methylvinylpyrrolidone or 2-hydroxyethyl methacrylate are examples of polymeric dispersants. Other types of ashless polymeric dispersants are ethylene-propylene copolymers which have been oxidized and then reacted with a polyamine, and ethoxylated polybutenephenol in which the terminal hydroxyl group is converted to an amine or polyamine.

Industrial Oils

The industrial oils that depend most on the performance of a surfactant are the soluble oils or emulsifiable oils used in metal working. In that application, the aqueous phase provides cooling whereas the oleic phase provides lubrication. Sodium sulfonates of both petroleum and synthetic origin are the surfactants of choice in this application. These sulfonates are similar to the sulfonates used in engine oils, but they are of slightly lower MW.

Aside from small amounts of corrosion inhibitors, frequently alkylsuccinic acid derivatives, most circulating oils contain no other surface-active additive. When surfactants are used, they are apt to be small amounts of calcium, barium or zinc sulfonates, phenates or salicylates. The volume of surfactants used in industrial oils should parallel the economy.

Grease

The main role of surfactants in grease is to thicken lubricating oil. Thickening is accomplished by means of a gel structure set-up among surfactant molecules. The most common surfactant thickeners are soaps of fatty acids. The most common soap is the lithium soap, accounting for over half the North American grease market. Second to lithium soaps are sodium and calcium soaps, then the aluminum soaps. Urea polymers and surfactant-treated clays also are used as thickeners in grease.

The primary function of grease is to provide lubrication as needed. Sometimes that lubrication is required at high temperature, for long periods of time, or under wet conditions. The best type of thickener or combination of thickeners depends on the conditions under which the grease is expected to function.

As with most petroleum products, greases also contain surface-active corrosion inhibitors.

Asphalt Emulsions

The principal market for asphalt emulsions is in road maintenance. Both anionic and cationic emulsifiers are used. Asphalt emulsions are designed to break rapidly or slowly when mixed with the aggregate, depending on the specification of the paving contractor.

Many different types of emulsifiers have been used in preparing asphalt emulsions. The most popular anionic emulsifiers are sodium soaps of petroleum acids generated either in situ with caustic or added as the preformed soap. The most popular cationic emulsifiers are alkyl amine or alkyl polyamine hydrochlorides and alkylamido polyamine hydrochlorides made from tallow acids or lignin.

Over the years, asphalt emulsions have been replacing asphalt cutbacks in road building. Rapidly increasing alternative use value of the cutter solvent in asphalt cutbacks and regulations against emitting large volumes of hydrocarbon solvent into the air have accelerated this trend. However, most asphalt emulsions and cutbacks are used on rural roads where air pollution regulations are less stringent than in the cities.

Drilling Muds

The largest and most complex use of surfactants in the oil field is in drilling muds. Of the many functions performed by drilling muds, surfactants contribute to the mud's ability to suspend drill cuttings and allow their transport to the suface, to control loss of fluids to the reservoir, to cool and lubricate the drill bit, and to reduce corrosion. Of the three types of drilling fluids, water-based, oil-based and gas-based, the water-based muds are used in greatest volume.

Surfactants in drilling muds act as thinners, emulsifiers, lubricants, foamers, defoamers and corrosion inhibitors. Thinners are added to drilling mud to help disperse the clay component of the mud. In keeping the clay dispersed, the thinners help control loss of fluid to the formation being drilled. Lignosulfonates are the most widely used surface-active thinners.

Emulsified oil in water-based muds helps lubricate the drill bit. Emulsified water in oil-based muds increases viscosity. Alkylaryl sulfonates and petroleum sulfonates are the principal anionics and ethoxylated alkylphenols are the principal nonionics used as emulsifiers in water-based muds. Calcium and magnesium salts of tall oil fatty acids are the principal surfactants used in oil-based muds.

Lubricity of water-based drilling muds also can be improved by adding a surface-active lubricant. Sulfonated asphalt and soaps of sulfurized vegetable oils are the most widely used surfactants for that purpose.

Sometimes foaming is desirable; sometimes it is not. Gas-based drilling fluids are intended to be foams, and the most commonly used foaming agents are alcohol ether sulfates and ethoxylated alkylphenols. In other drilling fluids, foam is undesirable, so surfactants such as aluminum stearate and sodium alkylaryl sulfonates sometimes are added to control foam. Finally, as with so many products manufactured by or used by the petroleum industry, drilling muds contain corrosion inhibitors. Fatty amines or their imidazoline derivatives are the most popular corrosion inhibitors in drilling mud.

Cements

In an oil well, the volume between the metal casing and the borehole wall is sealed with cement. Surfactants are used in preparing that annulus volume for cementing and in the cement itself as retarders, dispersants, fluid loss additives and defoamers. The first step in preparing the annulus for cementing is to remove the drilling mud. That is accomplished by pumping a "spacer fluid" or a "flush" down the casing and up the annulus. In addition to displacing the drilling mud, the spacer or flush must also condition the casing and the wellbore to improve adhesion of the cement. Petroleum sulfonates account for the largest volume of surfactant used in this application, but alkyl benzene sulfonates and some ethoxylated nonionics are also used.

Sometimes, particularly in hot, deep wells, the rate of setting of the cement must be retarded. Calcium lignosulfonates are by far the largest volume surfactant used as a retarder. Smaller amounts of glucoheptonates also are used as retarders.

Dispersants can be added to a cement to reduce its viscosity. Naphthalene sulfonates are used in greatest volume. The glucoheptonates also act as dispersants.

When the permeability of the formation is high, loss of water from the cement into the formation can alter the properties of the cement. Polyethylene amines are the principal surface-active materials used to reduce the amount of water lost to the formation. Naphthalene sulfonates also retard water loss from a cement.

A final use of surfactants in oil field cements is to reduce foaming during the mixing of the cement. Dibutylphthalate an lauryl alcohol are the most commonly used defoamers.

Completion Fluids

When the well reaches the oil-bearing zone, the drilling mud is often replaced by a completion fluid to minimize damage to the oil-bearing formation. One type of completion fluid, used occasionally in deep, hot wells, is a water-in-oil emulsion. The emulsifiers for such completion fluids usually are calcium sulfonates or calcium salts of fatty acids.

Water-in-oil emulsions, similar to those used as completion fluids, are used also as packer fluids. A packer seals the annular space between the well tubing and the well casing, and the packer fluid fills the space above the packer. Since the packer fluid may remain in contact with the tubing and casing for a long time, its ability to retard corrosion is an important property. Water-in-oil emulsions perform well in that regard.

Stimulation Fluids

Treating an oil well to increase flow is called "stimulation." The two principal stimulation methods are acid-treating and fracturing. The two methods can be used independently or simultaneously.

In acid-treating, strong acids are pumped down the well and into the formation to dissolve away part of the formation, thereby increasing its permeability. Surfactants are added to stimulation fluids to inhibit corrosion, retard reaction rate of the acid, aid in removing fines and spent acid. prevent emulsification and "wet" the rock. Surfactant types used in greatest volume as corrosion inhibitors in well-stimulating acids are the alkylpyridines and alcohol ethoxylates.

Retarders are used in well-stimulating fluids to slow down the rate at which the acid dissolves rock in order to penetrate deeper into the formation. One method of retardation is to emulsify the acid in keorsene. Petroleum sulfonates and fatty acid derivatives are the principal emulsifiers.

Another way to slow the rate of acidification is to foam the acid with nitrogen. Surfactants such as alkyl ether sulfates, ethoxylated alkylphenols, ethoxylated alkyl quaternary amines and fluorinated esters are used to stabilize the foam.

Ethoxylated alkylphenols and ethoxylated quaternary amines are used most frequently to aid in the removal of fines and spent acids after the acidification is complete.

Above-Ground Surfactants

Even after the oil is produced from the well there is continuing need for surfactants. More water than oil is produced from most oil wells, and that water must be treated before it is disposable. The oil frequently contains emulsified water which must be removed before the oil can be sent to the refinery. Surface-active demulsifiers frequently are added to the oil to help break such water-in-oil emulsions. Usually those demulsifiers are nonionic, such as ethoxylated alkylphenols and polyoxyethylene glycols. Less frequently, oil-in-water emulsions are produced, in which case the demulsifiers are likely to be cationic polymeric amines or their salts.

At some field locations, small amounts of oil are removed from water by foaming. Alcohol ether sulfates are by far the most widely used surfactant in that operation. Conversely, at some locations foams are a problem, so defoamers such as aluminum stearate, sodium alkylaryl sulfonates and fatty alcohols are used.

As it is throughout the entire petroleum industry, corrosion is a problem in oil production. Fatty amines, imidazolines and quaternaries are the most popular surface-active corrosion inhibitors used in the oil field.

Surface-active fatty amines and quaternaries are among the many different types of biocide used to treat the separated water before it can be reinjected into a reservoir.

Finally, surface-active scale inhibitors and paraffin dispersants find use in oil field operations. Organic phosphonates are the most popular scale inhibitors and ethoxylated nonyl phenols are the most popular paraffin dispersants.

Growth for Oil-Field Surfactants

Although oil production in North America is expected, at best, to hold constant throughout this decade, drilling activity is projected to remain strong. Furthermore, the average depth of new wells is increasing, and old wells are being kept on production longer. Although some experts believe that surfactants are over-used in stimulation fluids, the total market for surfactants in the oil field should increase during this decade.

It is likely that some surfactants in oil field use today will be replaced by new surfactants. There seems to be more room for cost-efficiency improvement in surfactants used in the oil field than in surfactants used in the more established refinery products.

Some oil-field surfactant markets will grow faster than others. For example, since the ratio of water to oil produced by the average oil well is increasing, surfactants used in separating and treating water should show better than average growth. Deeper wells mean hotter wells; so drilling mud surfactants that are stable at high temperatures, such as the lignosulfonates, should be in greater demand. On the other hand, environmental constraints may reduce the amount of chromium lignosulfonates used in drilling muds. Environmental constraints may also limit the quantity of surfactants used to emulsify oil in muds for offshore drilling.

Although the oil-field surfactant markets are forecast to enjoy substantial growth, the enhanced oil recovery market offers the greatest tentative potential.

Enhanced Oil Recovery

For every barrel of oil pumped from an oil reservoir, almost two barrels of oil on the average have been left behind. We do not have to look for that oil; we know where it is, but we do not know how to recover much of it economically. Such residual oil is the target for methods of enhanced oil recovery (EOR).

Sometimes, when the oil is quite viscous, more can be recovered by heating it with steam. More often, the residual oil is trapped in pores of the reservoir rock by capillary forces, so methods of enhanced recovery which lower interfacial tension are required. Other methods of EOR, such as carbon dioxide flooding, tend to swell the residual oil, thereby increasing the apparent oil saturation in the reservoir and reestablishing flow. Frequently, methods of EOR function by more than one mechanism.

EOR through lowering interfacial tension is an obvious use of surfactants. However, proper design of effective surfactant floods is difficult. One reason for the difficulty is that interfacial tensions must be very low—usually less than 0.01 dynes/cm. Such low interfacial tensions are a function of the type and concentration of surfactant, the temperature, the composition of the crude oil, the composition of the reservoir rock, and the salinity of the formation, make-up and drive brines. Compounding the difficulty is the need to maintain ultralow interfacial tension over a period of years as the surfactant bank moves through the reservoir rock.

Petroleum sulfonates and alkylaryl sulfonates are the principal "primary" surfactants used in EOR by surfactant flooding. In almost all formulations, the "primary" surfactant is supplemented by a "cosurfactant," such as an alcohol ethoxysulfate or an alkylphenol ethoxysulfate, or by a "cosolvent" such as a low MW alcohol or a low MW alcohol ethoxylate.

The economics of EOR by surfactant flooding do not permit use of enough surfactant to remove oil by emulsification and dispersion similar to removing oily soil from clothes in a washing machine. Instead, a small "slug" of surfactant solution must push oil ahead of it as it moves through the reservoir rock. To do that efficiently, the surfactant slug and the "drive" fluid which follows it must be provided with controlled "mobility." Although the mobility of a fluid flowing through rock is a function of both its viscosity and the "permeability" of the rock to that fluid, the concept of mobility control can be grasped by considering only viscosity.

If we attempt to push a liquid through a rock with another liquid of lower viscosity, the driving liquid will tend to channel or "finger" through the driven liquid. On the other hand, if the viscosity of the driving liquid is higher than the viscosity of the driven liquid, fingering will be negligible and displacement of the first liquid by the second will be much more uniform and complete. Therefore, for efficient surfactant flooding, the viscosity of the surfactant solution must be higher than the effective viscosity of the oil-water bank it is displacing, and the viscosity of the drive must be higher than the viscosity of the surfactant solution.

Mobility control in surfactant flooding is achieved almost exclusively with water-soluble polymers, hence the name "micellar-polymer flooding." (Surfactant concentrations in the slug always are above the critical micelle concentration.) Frequently, the surfactant slug and the microemulsions formed in the reservoir, as the surfactant slug mixes with crude oil and formation brine, are viscous enough to require no additional mobility control; but the drive always requires mobility control to be efficient. The most beneficial advance that could be made today in EOR by surfactant flooding would be a more reliable, less expensive way to control mobility of the drive. Possibly, surfactants will play a role in filling the need for better drives; surfactant-stabilized foams are being studied for that purpose.

Since the viscosity of supercritical carbon dioxide is even lower than the viscosity of water, mobility control can increase the efficiency of enhanced oil recovery by carbon dioxide flooding. Again, surfactant-stabilized carbon dioxide foams and emulsions are being studied.

The furthest advanced application of foams in enhanced oil recovery, now in the field development stage, is in steam flooding. Not only is the viscosity of steam low, but its density also is low. Consequently, steam fingers and also overrides the crude oil and brine in the reservoir. Steam foam produces a more uniform displacement on both counts.

Surfactants that are suitable for EOR by steam foam must be thermally and hydrolytically stable. Temperatures as high as 300-400 F (150-200 C) are common in reservoirs under steam flood. Leading surfactant contenders are alkylbenzene sulfonates and α-olefin sulfonates.

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The Use of Inorganic Sacrificial Agents in Combination with Surfactants in Enhanced Oil Recovery

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ABSTRACT

Current literature on optimization of surfactants in enhanced oil recovery is summarized. Effectiveness of the use of surfactants in chemical EOR processes is dependent on many factors. Uncontrollable factors such as reservoir parameters, minerology, and the nature of the crude oil influence the choice of a chemical process. Each reservoir offers a different set of problems to be solved. When the use of a surfactant is warranted, one attempts to optimize further the activity of this surfactant by modifying the chemistry of the reservoir system. Cost aside, maintenance of optimal surfactant activity is essential to minimize the oil/water interfacial tension. Also, loss of surfactant activity due to adsorption on substrate material is particularly disadvantageous because the water wet nature of the rock may be decreased. The use of alkaline, weak acid anions, such as sodium silicate, phosphate and carbonate to enhance surfactant effectiveness has been studied. These sacrificial agents can reduce the hardness (divalent cation) activity of the solution and compete with surfactant for active sites on the reservoir rock surface. Core flood results show that there is an inverse correlation between surfactant retention in the core and residual oil recovery. They also suggest that surfactants may be recovered for reinjection by the optimal use of sacrifical agents—in particular, the sodium silicates.

INTRODUCTION

Attention turns increasingly toward enhanced oil recovery (EOR) methods as the petroleum yield per effort of drilling decreases (1) (Fig. 1) and as production using conventional methods declines (2) (Fig. 2). The original flow of oil from the reservoir in primary and secondary recovery is less than perfect because of inefficiencies in fluid flow characteristics (physical displacement/sweep) and/or the chemical displacement of oil by the contacting fluids.

The fluid flow characteristics of oil are governed by reservoir permeability and porosity, oil viscosity and pressure gradient factors. For oil in contact with displacing fluids, the displacement efficiency is generallly enhanced by reducing the ratio of the viscosities of the oil and displacing fluid, reducing the density of oil, reducing the oil/fluid interfacial