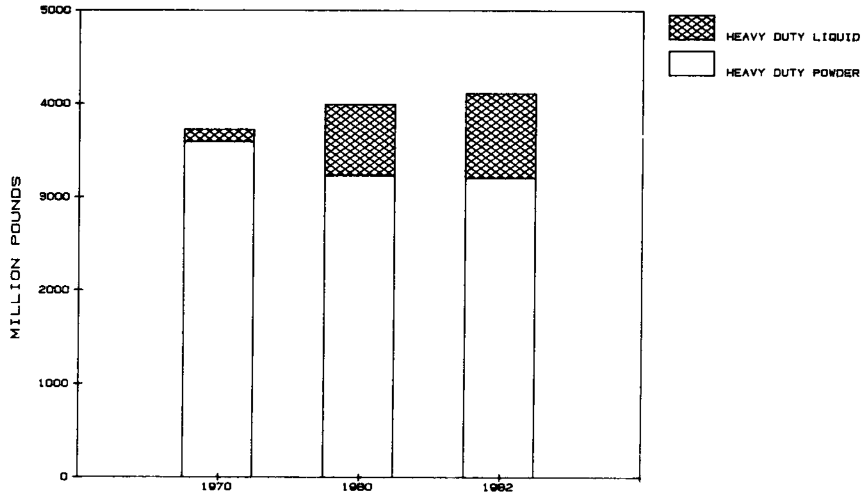

FIG. 8. United States trends in powder vs liquid heavy-duty detergents.

based surfactants than to that of LABS.

The total household powder and liquid market continues to grow, albeit at a low rate of 1-2% per year. Alkylbenzenes are static in the USA, but the alcohols have been able to increase their market share. This trend is expected to continue.

The market continues to evolve, further complicating the selection of surfactant systems. The introduction of enzymes in heavy-duty liquids, and the inclusion of wash cycle fabric softeners, are two progressing product developments that tend to favor alcohol-derived surfactants. Increased raw material costs and pressure to maintain prices at the consumer level breed a fiercely competitive environment.

All of the factors discussed in this presentation indicate that detergent alcohols, and natural alcohols especially, have a bright future in store. The important points in favor of the alcohols are a raw material base that can be opportunistically shifted between petroleum and natural oils, excellent biodegradability and excellent performance in detergent applications under today's conditions.

Marketing and Economics of Oleochemicals to the Oil Patch

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ABSTRACT

Oleoamines represent the largest class of oleochemicals used in the oil patch and are used in virtually all phases of the oil industry. Although the largest volume is used in production and refining, many amines are used prior to production in drilling operations and well completions, as well as postprocessing as additives in finished products. Other oleochemicals widely used include various surfactants made by ethoxylation and sulfation of fatty acids as well as polymerized fatty acids. The amines of interest start with simple primary amines and include secondary, tertiary and quaternary amines. They extend into higher amines such as diamines, triamines and beyond as well as all of these further reacted with other chemical species. Oleoamines in a generic sense also include amino amides, amphoteric amines, cyclic amidines, ether amines, as well as some high molecular weight polymeric materials. The oleoamines are used per se in suitable solvent systems, or as components in a wide variety of finished products containing several chemical entities to obtain specified product properties. Oleoamines, their derivatives, and other oleochemicals are used to prevent corrosion, inhibit and kill bacteria, condition waters for improved injectivity, emulsify, deemulsify, foam, gel, remove deposits, disperse solids, wet solids, solubilize or disperse otherwise incompatible liquids, produce or stabilize foaming systems, lubricate and produce detergent properties in liquid systems. They are used in drilling fluids. well completion fluids, oil and gas wells, water source wells, injection wells, gathering systems, filters, storage tanks, pipelines, refineries, and in finished products for all of the purposes listed above. This paper covers the oil patch operating parameters that determine the need for using oleochemicals, and describes for each system appropriate oleochemicals whose properties satisfy those needs.

The "oil patch" is not one industry, but many. Generally, the applications are grouped into three general areas: exploration, production and refining. This discussion will begin with the drilling of the well and take the reader through numerous steps necessary to obtain finished refined products.

OIL AND GAS WELL DRILLING

Oil Muds

A high-grade Wyoming bentonite is reacted with a quaternary ammonium chloride made from methyl dihydrogenated tallow amine. Bentonite, by nature a water-swelling clay, is converted to an oil-swelling mixture. This product is the basic component for many oil muds.

Historically, the oil mud market has been only 10% of the total market. Due to the economics, water-base muds have had a 90% market share. Recent surveys of major oil companies and major mud companies indicate that oil mud usage is increasing and may eventually become a 30% factor in the total market. The reasons for this increase in market are as follows.

Deep drilling. Oil muds are more heat-stable, thus find a larger application as deeper drilling becomes more prevalent. The extent of deep drilling appears to have established a trend. Deep wells, 15,000 ft or below, accounted for a 400-600 well average during the late 1970s. This figure reached 989 wells in 1981. In 1982, despite a worldwide recession, there were 1,299 deep wells drilled. Although deep drilling at this rate accounts for only 2-3% of the holes drilled, it accounts for ca. 25% of the total mud market.

Slant hole drilling. Offshore fixed platforms are now capable of handling 50-60 wells. Some of these wells deviate out to 70° off the vertical. Although depth may not be considered great, oil mud is used to a great extent because of better lubrication and hole stability.

Faster penetration holes. These are obtained with oil muds due to less torque on the pipe (lubrication) and keeping the bit clean.

More economical. Oil muds are often more economical than water-based muds in the drilling of certain types of formations. Less stuck pipe, less sluffing of shale, and generally better hole conditions are expected with oil muds. In addition, at times, oil mud eliminates the use of protective casing. You may stay in an open hole longer with oil mud.

Arctic regions. Here, oil base muds are ideal for application. The prime reason, of course, is because they do not freeze, as do water-based muds. Drilling wells from ice islands have great potential. Currently there are some environmental problems using oil mud in the conditions described above, but it is felt that they will be overcome.

Other special uses. These include well workovers, completions and spotting fluid.

Other chemicals used in oil muds are: fatty acid salt of diethylenetriamine, diethanolamine, diethanolamide, imidazoline/amide mixtures, tetraethylene pentamine, triethylene tetraamine, reactions of the above amines with fatty acids to produce amido amines.

Other applications in drilling include (a) foaming agents – numerous oleyl surfactants are used in air and gas drilling to foam H_2O and carry drill cuttings out of the hole; and (b)corrosion inhibitors – imidazolines and fatty amines are used to prevent corrosion of the drill pipe in many corrosive conditions.

WELL COMPLETIONS

Acidizing

A large amount of oil and gas is produced from formations consisting predominantly of limestone ($CaCO_3$) and dolomite $CaMg(CO_3)_2$. Acidizing is an important method used for the stimulation of wells drilled in these formations. The acid, which is generally a 15% HCl (maybe up to 33%), is injected into the producing formation under pressure. Acid plus surfactants dissolve the matrix and generally "clean up" the surrounding surface area of any acid-soluble material impeding the flow of oil or gas toward the well bore. Some acid jobs are done under high pressure to create a rupture or fracture in the producing formation. At other times, it is necessary to inject under low pressure to prevent a vertical fracture into a water zone. The strength of acid, the viscosity, the fluid makeup, and many other variables along with pressure and time must be taken into consideration. Specific uses for oleochemicals are as follows.

Corrosion Inhibitors

Derivatives of imidazolines ans straight-chain fatty amines are formulated usually with acetylenic alcohols to obtain an HCl inhibitor. The inhibitor prevents corrosion not only in the high pressure truck and injection equipment but more importantly prevents metal loss in the down hole tubing and casing.

Surfactants

Oleochemicals used either as a pretreatment or with the acid job may include quats, fatty amine and/or fatty acid derivatives.

Emulsifying Agents and Gelling Agents

A number of oleochemicals are used for gelling acid and water, acid and oil, etc. As could be expected, soaps are predominant as gelling agents. Various fatty amines and quaternaries are used as emulsifiers, along with soaps and nonionics.

Deemulsifying Agents

HCl sometimes reacts with certain crude oils to produce emulsions which plug or severely restrict oil or gas flow within the formation. Many deemulsifiers and surfactants are used to prevent these emulsions or to break them should they be formed.

Other uses for oleochemicals may include: fluid loss additives, friction reducers, clay stabilizers, foaming agents, and paraffin inhibitors.

Hydraulic Fracturing

Fracturing is another important method used to improve production of an oil or gas well. Simplified, it is a process whereby a viscous sand-suspending fluid is pumped under high pressures into the producing zone. The formation rock is forced to split or shatter, the fluid drains back into the well bore leaving in place the sand holding the fractures open. The object, of course, is to increase the drainage of oil and gas into the well bore.

Fracturing fluids vary greatly with the conditions. They may be oil-based, water-based; may achieve their sand-suspending qualities by the formations of an emulsion or a gel – or virtually any method to increase the viscosity of the fracturing fluid. The fluids may or may not include HCl.

Emulsifiers

Several oleochemicals are used to emulsify oil and water, thus increasing the viscosity and sand-suspending properties of the fluid. Once in place in the reservoir, the emulsifier (usually cationic) breaks due to being absorbed on the "electronegative" surface area of the reservoir, the fluid then draining back to the well bore. Fatty amines and their derivatives are often used as the emulsifier. Soaps of fatty acids are used in this application – again as emulsifiers and surface-active agents.

At times, produced water from the lease is used as a component in the fracturing fluid. In such cases, it is wise to treat the water with a biocide to inhibit or kill sulfate-reducing bacteria.

The market for oleochemicals used in drilling, acidizing and fracturing is believed to exceed $150 million per year.

PETROLEUM PRODUCTION

Almost all of the problems associated with the production, processing, storage and transportation of oil and gas that necessitate the use of oleochemicals are caused by the presence of water and the materials dissolved in the water. The waters produced are infinitely variable, containing from a few tenths of a percent salts and traces of gases to more than 30% salts and percent level gases that are corrosive, scale-forming, and capable of producing suspended solids.

Producing wells vary from natural gas wells containing essentially no liquids, to gas plus liquids, to oil wells producing all liquids. They vary from depths as shallow as 200 ft to as deep as 5 miles and are under pressures from zero to over 20,000 psi. Varying amounts of water containing the dissolved materials requiring the use of oleochemicals are produced along with the desired oil and gas. The net result is that oleochemicals used to overcome the operating difficulties must be able to function in whatever environment is present in the well system being treated. This requirement alone leads to a very large number of products containing specific ingredients to control specific aspects of producing mechanics. The world market for corrosion chemicals alone is estimated at $150 million. Oleochemicals are included in most of the complex formulations used for corrosion prevention. Fatty amines such as tallow diamine, oleyl diamine, etc., as well as imidazolines, amino amides, plus fatty acid salts of all of these and quats are included in corrosion inhibitor formulations. Other oleochemicals required for controlling solids, modifying product solubilities, and/or providing detergent properties include ethoxylated fatty products such as the amines, imidazolines and a great many other surfactants using fatty acids as the starting material. Polymerized fatty acids as well as simple mono fatty acids are used to make salts of the inhibitor base materials (amines, etc.) to enhance specific properties of those base materials.

Another major set of problems associated with producing well systems are those caused by the presence of bacteria in produced fluids. Bacteria are troublesome because they form deposits that restrict flow and add to already existing corrosion. They also create suspended solids that aggravate emulsions and plug water disposal or injection wells. Almost all of the biocides used to treat oil wells are water-soluble and, in fact, similar to products used as disinfectants in other applications. Oil wells plagued with bacteria are usually treated by injecting biocides down the annular space between the casing and producing tubing. Treatment can be continuous or periodic batch to control growth with occasional high concentration slug to kill. The major effect of the bacteria in oil wells is on corrosion. In disposal or waterflood injection wells, however, the major problem is the plugging. Oleochemicals used include both methyl and benzyl quaternary ammonium chlorides, sulfates and acetates derived from C_{12}-C_{18} fatty amines. Examples are coco dimethyl benzyl ammonium chloride, soy trimethyl ammonium chlorides. Other products include coco diamine acetate and other alkyl amine salts. The market for such products worldwide amounts to $55-60 million per year. Oleochemicals account for ca. 50% of this market.

As producing oil wells age, production drops for various reasons. Some of the causes of the decrease in flow can be overcome by various treatments referred to as stimulation. Sometimes flow restriction is caused by the accumulation of inorganic scale. At other times, bacteria and deposits restrict flow. Corrosion products or solids from the producing formation itself can also be flow restricting. Acids play a major role in well stimulation but emulsion breakers, surfactants, and biocides derived from oleochemicals are also used in substantial quantities. The market for chemicals used in well stimulation worldwide is estimated to be $100 million annually with the oleochemical share ca. 10-20%. Products are often mixtures of several materials from such bases as fatty acid ethoxylates, fatty amine ethoxylates, ethoxylate-sulfates and quats.

As crude is removed from oil reservoirs, production will drop off with time because the fluids and gas removed lowers producing zone drive pressure. To prevent rapid decline and to produce more of the oil from reservoirs, various methods of enhanced oil recovery under the classification of secondary and tertiary recovery are used. Steam, gas and water are injected either separately or in combination along with various chemicals to effect reservoir pressure and drive maintenance. If water is the material being injected, the process is called water flooding. Oleochemicals are used extensively in the process. Whereas a majority of the oleochemicals used in producing systems are soluble in oil, those used to treat injection waters must be water-soluble. The waters used must be conditioned for corrosion, for control of bacteria, for solids removal, for removal of residual oil, and for surface tension reduction to improve injectivity. Thus, water-soluble versions of amines, imidazolines, quats and surfactants of various kinds derived from oleochemicals are required. The market for these products is estimated to be $60-70 million per year, of which ca. $20 million is oleo-base material.

From the producing wells, crude oil and gas go to separation facilities where the water is removed. However, because of limited time in the separators, some water remains in the oil to separate with time and settle to the bottoms of storage facilities. The result is a continuation of the problems associated with the presence of the water in the production facilities. Often additional oleochemicals of the same types used in producing facilities must be added to products in the storage facilities. In this case the emphasis is on water-soluble products. For example, in the producing well the primary corrosion inhibitor may be either tallow diamine (oil-soluble) or tallow diamine acetate (water-soluble). In storage tanks, the water-soluble version must be used.

Transportation systems, and in particular pipelines carrying crude oil as well as those carrying natural gas or gas already processed and ready for consumer uses, still often require chemical treatment. For the crude oil pipelines, the emphasis is on the use of chemicals designed to reduce resistance to flow and those used to prevent corrosion. The flow improvers are oil-soluble but the corrosion inhibitors must be extremely water-soluble. The reason for the later is that almost all of the corrosion in a pipeline carrying crude oil occurs in the bottom in low spots where water separates and remains more or less static. Any product with appreciable oil solubility would be mostly unavailable to the corrosion sites in the water layers because of the much larger ratio of oil to water in the system. The consequence of this is that oleochemicals used as base materials for these purposes are C_8-C_{10}. It turns out that the costs of these fractions approach the costs of synthetic C_8-C_{10} alternative raw materials so the oleochemical use is smaller than it could be (availability aside).

Pipeline systems carrying gas use special corrosion inhibitor formulations containing both C_8-C_{10} water-soluble oleo-based materials and C_{12}-C_{18} oil-soluble materials. This is necessary because the gas can actually contain both liquid hydrocarbon and liquid water in different areas to where corrosion inhibitor must be carried. Thus a gas pipeline inhibitor may contain a tallow imidazoline for the oil phase and a C_8-C_{10} amine for the water phase.

Pipelines carrying finished products must be treated with products with even more controlled properties. All of these products must be very high quality and maintain complete long-term solubility in the hydrocarbon system being treated. The oldest corrosion inhibitors used in jet fuels are polymerized and purified fatty acids.

PETROLEUM REFINING

Antifouling

Once the crude oil reaches the refinery, it is pumped through large exchangers to pick up heat from distilled products leaving the unit. The crude oil contains many types of contaminants such as water, dirt, wax, sulfur and polymers. These materials tend to stick to the surfaces of the exchanger and eventually plug or restrict the flow and lower the efficiency which can be measured in terms of dollars from lost energy. These deposits also create differential heat spots which contribute to increased corrosion rates in the exchanger. The premature loss of the exchanger is a major expense; however, the most serious loss can be the downtime on a crude unit. Antifouling agents must have excellent detergent, dispersing and film-forming properties and function at high temperatures. Long-chain fatty amines and ethoxylated imidazolines are often used in these formulations which are injected continuously into the systems at very low dosages of 5-20 ppm.

Desalting

Crude oil arriving at a refinery has generally been treated to remove the bulk of water but it may contain up to 1.0% of water and salt. This salt is removed by mixing the crude with fresh water to extract the salt. The tight emulsions that are formed must be broken so that the crude is freed of the salt bearing water. A strong electrical field is applied to the crude to break these emulsions but a chemical demulsifier is generally used to enhance the demulsification process. The advantages of using these desalting compounds are: less salt and other water-soluble contaminants in the crude, better desalter performance due to a decreased emulsion interface and effluent water nearly free of hydrocarbon. Oleochemicals are sometimes used as a part of the demulsifier formulations.

Demulsifying

Hydrocarbons and water are in intimate contact throughout most of the refining process; desalting of crude, steam distillation and water washing of treated product are just some of the possibilities to form emulsions. The skimming of water, draining of tanks and other operations result in the accumulation of large quantities of emulsified oils. Although not a large consumer of demulsifying chemicals, there is a requirement in the refinery for a tank type treatment of oil for demulsification. By far the largest requirement for a demulsifier in the refinery is to obtain clean separations of water and hydrocarbons in the receivers after distillation. In application a chemical which functions both as an inhibitor and/or antifoulant and demulsifier is desired. Long-chain amine derivatives and fatty acid triethanolamine condensates are effective for this purpose.

Corrosion Protection

Fatty amines, imidazolines and amino amides are used in the overhead of distillation columns to reduce corrosion. Along with pH control to neutralize HCl formed, these inhibitors form films which protect the metal surfaces especially at the vapor condensation point.

Total market in the refineries of oleochemicals is estimated to be in excess of $125 million. The US market for transportation systems additives is $50-60 million. Oleochemicals capture ca. 25% of these markets.

TERTIARY RECOVERY

Finally, there is a very large potential market for oleochemicals that will develop when present, mostly experimental, enhanced oil recovery (EOR) projects are converted into full-blown standard practice. In a Bartlesville Energy Technology Center report of "Chemicals for Enhanced Oil Recovery" published in April, 1981, estimates of fatty acid derived surfactants volumes that could be used in EOR projects would exceed the available supply capacities of all the sources of suitable fatty acids. Simple soaps and ethoxylates of oleic acid are mentioned prominently. Extrapolation of some of the numbers presented indicate the potential market for oleochemicals in EOR could amount to over a billion dollars per year if it proceeds as outlined. How quickly the EOR market develops for oleochemicals and how large it actually becomes will be determined by the economics. Current markets are very small.

Marketing and Economics of Oleochemicals to the Plastics Industry

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ABSTRACT

The number of oleochemicals used in the plastics industry are many and varied. Usually the chemicals sold are designed for a specific application that depends on the end use and the economics of production. The percentage of oleochemicals that end up in the finished product is small, usually 0.1-1%, but it is there for a very important physical specification that the chemical imparts to the finished resin. The chemicals and applications are discussed by the structure of the additive and the property it imparts to the finished resin. The marketing of oleochemicals to the plastics industry usually requires considerable application and process research to develop specialized molecules that impart the desired properties to the finished resin. Market size and economics numbers refer only to the US markets.

SLIP AGENTS–FATTY AMIDES

Primary fatty amides of C_{18-22} carbon atoms are the dominant slip agents used in polyethylene and polypropylene resins (1,2). The main compounds are either octadecenamide. The products function because, after the primary amides are dissolved in the resin, the polar group, on cooling, orients to the surface of the nonpolar resin which then forms a monomolecular film on the resin surface which allows the solid resin to be antiblocked or slip across an attached resin surface. The end result is the same as wax-coated or resin-coated papers which allow one resin surface to slide horizontally across another. An amide concentration of only 0.1-0.5% is used in plastic films. Since most of the polyolefin film is used in food wrap, the primary amides are approved under FDA Regulation 121.2509.

The simple amides used in this application are produced by the reaction of fatty acids or esters with anhydrous ammonia under pressure (3), according to the following equation.