

## Review Article

# REVIEW OF OILFIELD CHEMICALS USED IN OIL AND GAS INDUSTRIES

### ABSTRACT

The petroleum industry includes the global processes of exploration, extraction, refining, transportation and marketing of natural gas, crude oil and refined petroleum products. The oil industry demands more sophisticated methods for the exploitation of petroleum. As a result, the use of oil field chemicals is becoming increasingly important and has received much attention in recent years due to the vast role they play in the recovery of hydrocarbons which has humongous commercial benefits. The three main sectors of the petroleum industry are Upstream, Midstream and Downstream. The upstream deals with exploration and the subsequent production (drilling of exploration wells to recover oil and gas). In the Midstream sector, petroleum produced is transported through pipelines as natural gas, crude oil, and natural gas liquids. Downstream sector is basically involved in the processing of the raw materials obtained from the upstream sector. The operations comprises of refining of crude oil, processing and purifying of natural gas. Oil field chemicals offers exceptional applications in these sectors with wide range of applications in operations such as improved oil recovery, drilling optimization, corrosion protection, mud loss prevention, drilling fluid stabilization in high pressure and high temperature environment, and many others. Application of a wide range of oilfield chemicals is therefore essential to rectify issues and concerns which may arise from oil and gas operational activities. This Chapter intends to highlight some of the oil field chemicals and their positive applications in the oil and gas Industries.

**Keywords:** Oil field chemicals, Petroleum, Enhance oil Recovery, Demulsifiers, Corrosion

### 1. INTRODUCTION

The oil and gas provide more 60 percent of their daily energy needs of world. It is considered the biggest sector in term of dollar value and is the highest employer of labour in the world. They are so dynamic they contribute a significant amount towards national GDP. Nevertheless the Oil and gas industry is extremely effective and still experiencing enormous growth. The annual global energy consumption is estimated to be over 30 billion barrels predominantly by the industrialized nations. Oil and gas are vital to many industries and for civilization as it is the indispensable energy source for transportation and chemical production. Its consumption is 32% for Europe and Asia, 53% for Middle East, 44% for South and Central America, 41% Africa,

40% for America and 25% for United states of America. Natural gas is increasingly used for power generation as utilities look to switch to lower-emissions fuels, gas will overtake coal as the world's second-largest fuel in about a decade. Numerous issues arise which relates to Production chemistry which may be due to the physical and chemical changes in well stream fluids as they are conveyed from the reservoir via the processing system. The fluids from the wells usually contains complex mixtures of hydrocarbons (Natural gas, condensates and crude oil), and associated water. The mixture is transported from the reservoir through tubular string and wellhead through the flowlines to the processing plant for proper separation of the different phases. During the operations, change in temperature, pressure drop, and constant agitation will impact on the efficiency of the overall operation which may or may not be predictable. During the Downstream processing plant operation, the crude oil is transported to the refinery, the gas will be processed, while the water is treated to remove contaminants: in most case the processes can lead to additional problems. Most of these processes from the upstream to downstream requires the application of chemicals for effective delivery operations.

## **1.2 OILFIELD CHEMICALS AND SOME OF ITS APPLICATIONS**

Oilfield chemicals are chemicals used in petroleum production, processing and transportation. They are applied in operations such as drilling, completing and producing oil and gas wells. Relatively, the activities and operations in the oil and gas industry are reliant on the oil field chemicals to accomplish definite functions in the wellbore or formation. These oilfield chemicals include common inorganic salts, common organic solvents, transition metal compounds and their complexes, water-soluble and oil-soluble solvents and several others.

The alterations that takes place in the well stream fluids make oil field chemicals imperative by oil and gas plants.

### 1.2.1 Numerous oilfield chemicals used in the oil and gas industries includes:

- Corrosion inhibitors – reduce corrosion
- Scale inhibitors – reduce scaling
- Demulsifiers – speed up oil and water separation; dehydrates oil
- Water clarifiers–Clean up water before disposal.
- Hydrate inhibitors – Prevent ice-like hydrates
- Asphaltenes inhibitors – Prevent asphaltenes (large molecule) precipitation.
- Acid stimulations – removes acid soluble rocks and scale
- Drag reducers – improves flow through pipelines by reducing turbulence
- Sand control chemicals–reduce undesirable sand production from the wellbore.
- Napthenate inhibitors – stop precipitation of Ca/Na salt of naphthenic acid
- Wax inhibitors – prevent wax deposition
- Foamers – Reduces the density of fluids in hydrostatic heads
- Biocides - destroy microbes, prevents corrosion
- Hydrogen sulphide scavengers - react with toxic H<sub>2</sub>S gas, corrosion control
- Oxygen scavengers -- reduces oxygen levels, prevents O<sub>2</sub> corrosion

### 1.3 Drilling fluids

Drilling fluids are combinations, mixture or blends of natural and synthetic chemical compounds used to cool and lubricate the drill bit, clean the hole bottom, carry cuttings to the surface, control formation pressures, and improve the function of the drill string and tools in the hole [1].

Drilling fluids can be broadly classified into two main categories: water-based drilling muds

(WBMs) and oil-based drilling muds (OBMs). A drilling mud is distinct type of drilling fluid used for drilling deep oil wells. Some of the major functions of Drilling fluids includes regulation of downhole formation pressures, overcoming the fluid pressure of the formation, ensuring that the producing formation is not damaged, removal of drill bit cuttings from the borehole, and helping to cool and lubricate the drill bit [2, 3]. There are some factors to consider in the classification of drilling mud. These includes the kind of chemicals used in the preparation or formulation of the drilling mud, the dispersing properties and a combination of additional properties can be used to classify drilling muds as water-based mud (WBMs) contains or oil-based muds (OBMs). The water based muds contain water as water as the continuous phase while the oil based mud contains oil as the continuous phase.

Due to the ability of potassium ( $K^+$ ) to bind to clay surfaces and impart great level of stability to shales which are exposed to drilling fluids by bits, it is used in drilling water sensitive shales. More also, the ions also aid to bind the cuttings together thus reducing its dispersion to smaller particles. Potassium can be obtained from the following: Potassium chloride (KCl), potassium acetate ( $CH_3COOK$ ), potassium carbonate ( $K_2CO_3$ ), potassium hydroxide (KOH) and potassium salt of partially hydrolyzed polyacrylamide (PHPA).

Different types of polymers are employed for rheological control, these includes xanthan gum and PHPA. Chemicals such as combinations of starch and polyanionic cellulose (PAC), Carboxymethyl starch, hydroxypropyl starch, carboxymethyl cellulose (CMC) are employed as fluid loss control. Sodium chloride (NaCl) is main constituent of salt water muds, starch and its by-products are used for fluid loss control, and xanthan gums for hole cleaning are among the few additives that are effective for salt water muds.

In offshore drilling, sea water mud which is WBM is used. Sodium hydroxide (NaOH) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) are used due to the presence of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions which causes hardness. The ions are removed and precipitated as magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) and calcium carbonate ( $\text{CaCO}_3$ ).

Fluids whose density varies with pressure during drilling operation are known as variable density fluids. They usually have base fluids and elastic particles which are a copolymer of styrene and divinylbenzene, a copolymer of styrene and acrylonitrile, or a terpolymer of styrene, vinylidene chloride, and acrylonitrile [4].

Water-based mud (WBMs) have fundamental components such as Polyacrylamide, carboxymethyl cellulose, Acrylamide copolymer, polypropylene glycol (PPG) [5].

Efficient lubricating properties are achieved by combining Glycol or glycerol with anionic and cationic fluids which acts as inhibitor to swelling and dispersing of shales.

The viscosities of oil based muds (OBM) are commonly enhanced by using ethylene-propylene elastomers and Polyolefins (PAOs) due to their excellent properties such as good viscosity and pour point, biodegradable and being harmless to marine organisms are used in the formulation of OBM [6, 7].

Numerous naturally occurring polymers are added to drilling fluids to prevent fluid loss. Most of these polymers are susceptible to microbial degradation during drilling operations. Quaternary ammonium salts are used mostly used to protect the additives from biodegradation and reduce consumption rate during drilling deep wells. Bacterial control is also important in drilling fluids, and other oil and gas operations [8]. Some of the structures of chemicals used for bacterial control (bactericides) or biozides recommended for drilling fluids are shown in figure 1.

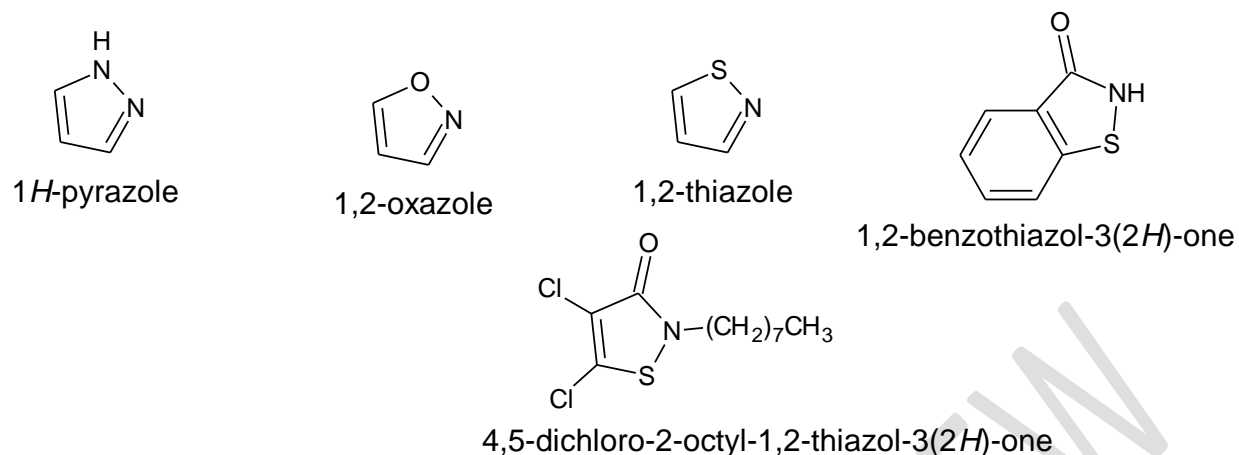


Figure 1.. Structures of components of bactericides or biozides

Some chemicals like Hydrazine are used as corrosion control in drilling operations and cementing due to its ability to remove oxygen. Such chemicals are called oxygen scavengers. A good example of such chemical is hydrazine [9].

Because of the excellent properties of naturally occurring calcium bentonites, they are used to enhance the viscosity of numerous drilling fluid. Their characteristics can be improved by blending with sodium carbonate to upgrade its quality to sodium bentonite which has superior viscosity performance characteristics. Alkylsilanes and phosphonates are used to modify the dispersing properties [10].

#### 1.4 Surfactants, Dispersants and Deflocculants

Surfactants (surface-active agent) are compounds that has the ability of lower surface tension between two liquids, a gas and a liquid, or liquid and a solid. They can be natural or synthetic. The presence of functional groups in the surfactants provide specific performance properties for a plethora of valuable industrial and consumer uses.

A dispersant or a dispersing agent or a plasticizer is a surfactant added to a suspension, (usually a colloid) to enhance the separation of particles and prevent settling. They can be a mixture of one or more surfactants, with the aim of reducing oil-water interfacial tension.

Surfactants like Methyl-diethyl-alkoxymethyl ammonium methyl sulphate applied as hydrocarbon solvent have properties that can extinguish foam. Other like Alkylpolyglucosides (APGs) which are biodegradable can be added to polymer muds to reduce fluid loss, enhance rheology and temperature resistance [11, 12].

A major characteristics of Chemicals used as Deflocculants is that they should have a low molecular weight. The dispersant used in dispersing bentonite suspension are complexes of tetravalent zirconium with some organic acids (citric, tartaric, malic, and lactic acids), and a complex of aluminium and citric acid have proved to be good dispersants. Furthermore, polymers composed of sodium styrene sulfonate and Organophilic clays can be treated with a quaternary ammonium surfactant having an amide linkage [13, 14, 15]. Examples of such surfactants are shown in Figure 2. They are a type of cationic surfactant that is significantly biodegradable, that is easily broken down by microorganisms in the presence of oxygen. Modified clay which are treated can be used in drilling fluids without apprehension of the likelihood of the surfactant contaminating the environment.

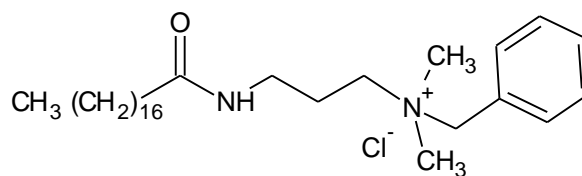
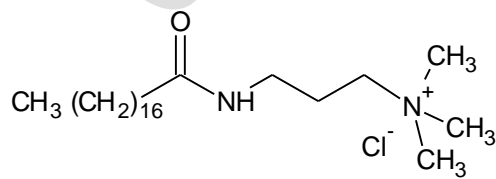


Figure 2 Quaternary ammonium surfactants

### 1.5 Cuttings, Junk and Filter Cake Removal

Chemicals like Barium sulphate are ground, filtered and suspended in drilling fluid to get rid of cutting beds. Cutting beds are deposits of small size drill cuttings that build up at the lower side of the wellbore when drilling horizontal wells. It is added to the drilling fluid and circulated in the wellbore to remove the small cuttings or cutting beds from the borehole and transport them to the well surface. A mixture of Nitric and hydrochloric acid in a ratio 1: 3 can be used to dissolve drilling equipment that is broken or stuck in hole. The dissolution of the metal is accelerated by adding a mixture containing 1.1 parts of sodium nitrate and 1.0 part of monoethanolamine. Further addition of an alkali and polymer solution neutralises the acidic residue and then converts the mixture into a drilling fluid [15, 16].

Circulation of the drilling fluid leads to the formation of a solid layer known as a filter cake on the walls of the wellbore. Preflushes are special chemicals which contain surfactants usually introduced to mitigate the problem of filter cake formation. An aqueous chemical wash solution contains sulfonated bisulfite lignin, and a taurate, present in amounts of 0.1– 5% [17]. Examples of taurates useful for preflushes are N-methyl-N-cocoyl taurate, N-methyl-N-palmitoyl taurate, and N-methyl-N-oleyl taurate and their metal salts (Figure 3). They are obtained by the acylation of N-methyl taurine with the corresponding long chain acids [18].



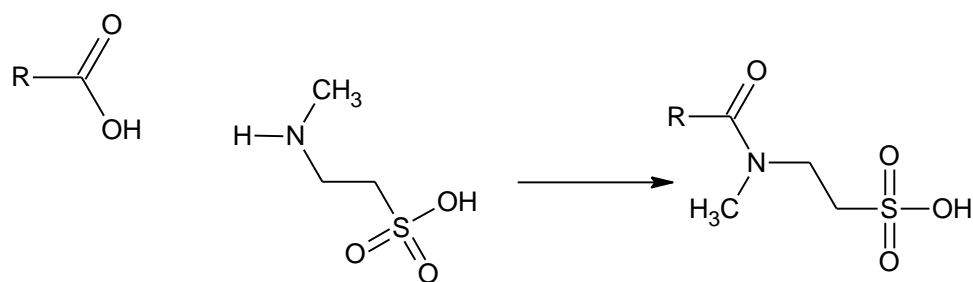


Figure 3. Acylation of N- Methyl-taurine.

## 1.6 Transport of Petroleum and its products

Pipelines are essential to the petroleum and gas industries for the transport of natural gas, crude oil and refined products. Chemicals and additives are used to ease the conveyance of these materials from one location to another. A lot of corrosives like Carbon dioxide (CO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S), water emulsified in the crude oil, naphthenic acids are the main cause of corrosion problems. They can also cause problems during refining, and processing [19]. Chemical additives are added to alleviate these problems. For example ammonia (NH<sub>4</sub>), Hydrogen fluoride (HF) and occasionally carbon monoxide (CO) are added to natural gas to be conveyed through pipelines. Treatment with alcohol like methanol reduces the naphthenic acid content, these leads to ester formation.

Gas hydrates are undesirable compounds produced during production or transportation of natural gas at low temperature and pressure. They are crystal-like or ice-like compounds of gas molecules in water, which form at low temperature and high pressures. More attention is attached to Gas hydrates in the petroleum industry due enormous problems they pose. Such problems includes blockage of drilling equipment, flow restriction in pipelines, valves, or

production equipment in which wet gas or multiphase mixtures are transported over long distances; as occurs in colder regions or on the seabed [20].

Gas hydrate can be prevented from forming by using moderately enormous amounts of lower alcohols such as methanol, glycol, or diethylene glycol. The main problem with hydrate formation arises in pipelines that transport natural gas, because they are solids and deposit. Chemicals such as polyethylene oxide in its aqueous solution, alkylated ammonium, phosphonium, or sulfonium compounds and amino acids or amino alcohols can be added into a drilling fluid to inhibit and interfere with formation and growth of gas hydrates [21].

Odorizers are added to natural gas to let its presence to be perceived in the environment before it reaches explosive levels. Few examples are ethyl mercaptan, diethyldisulphide and mixture of ethylmercaptan, propylmercaptan and butylmercaptans. The most important compounds are given in Figure 4.

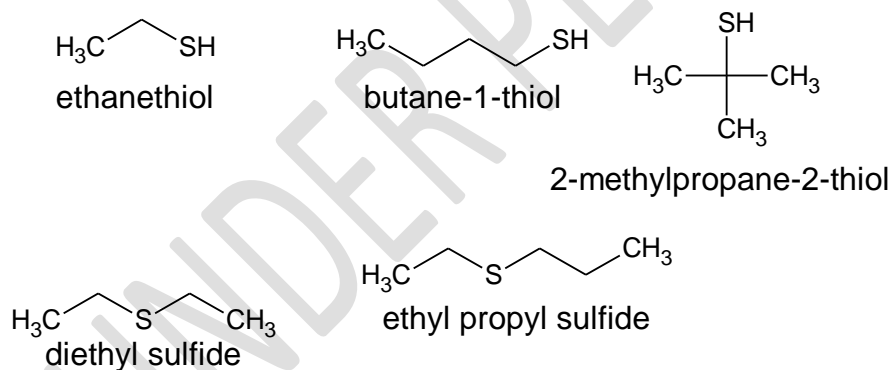


Figure 4, Structures of additives used for Odorization

Many anionic, cationic and non-ionic surfactants are used to remove solid materials produced during well drilling, polishing and gridding metals. Examples of such surfactants are

cetyltrimethyl ammonium chloride, dodecyl diphenyl oxide disulfonate, and soya bis[2-hydroxyethyl]amine [22].

There are some parameter that should be put into consideration when heavy crude oils is being transported. Some of these include velocity, viscosity, temperature, density, and pour point.

Chemical treatment of the heavy crude oil helps to activate the natural surfactants present in them [23, 24]. The method of chemical treatment is more effective than heating or diluting crude oils which have high viscosity. Carboxylic acids which are constituents of crude oils are the surfactant's precursors. Aqueous buffer solution of sodium hydroxide with sodium bicarbonate or sodium is used for activation [24, 25]. During low temperature transportation, inorganic salts, such as aluminium nitrate can be used in small quantities (30 ppm) are additional stabilizers for the emulsion [26]. In addition to the surfactants used in low temperature transportation, chemicals such as salts, sugars and glycerol can be added as freezing point depressant [27].

### **1.7 Pour Point Depressants and Chemical Inhibition**

The wax content of some crude oils are very high and they tend to pose problem during their transportation through pipelines especially in cold regions due to their high pour points.

Chemical inhibitors are nitrogenous complex mixtures used in oil production. There are different classes of Inhibitors such as oil-soluble, water-soluble or dispersible. The basic functions of chemical inhibitors is that they are film formers which protect the pipeline surfaces. A few examples are shown the figure 5

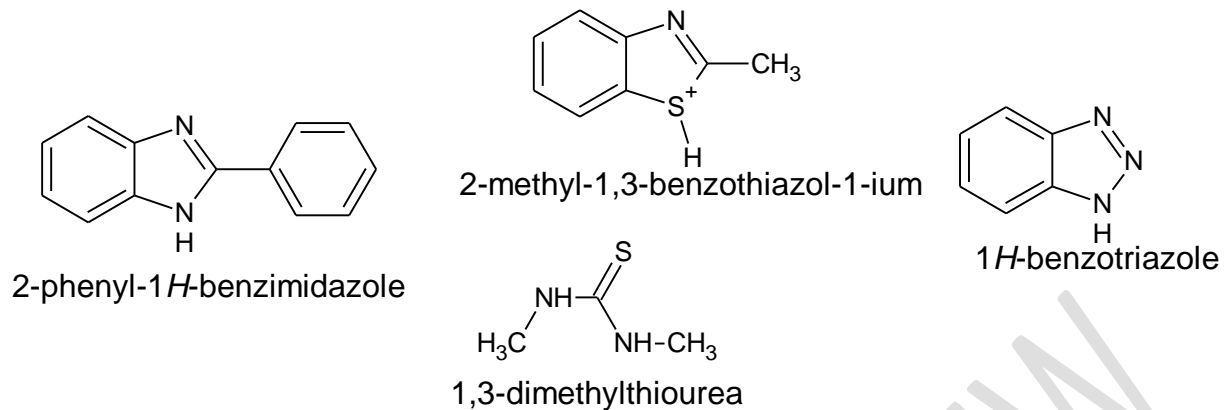


Figure 5. The structure of Corrosion inhibitors used in oil production

### 1.8 Corrosion Inhibitors

The deterioration of a substance, especially metals or its properties due to their reaction with interact with the environment is known as corrosion. Corrosion can lead to failure of operational processes in the oil and gas. Plate 1. shows the effect of corrosion on metal pipes.



Plate 1. The effect of corrosion on metal pipes

Corrosion inhibitors are oilfield chemicals that control corrosion of all facilities used during exploration and production of petroleum. They control internal and external corrosion of

downhole tubing and equipment, surface and sub-sea pipelines, pressure vessels and storage tanks. Electrochemical corrosion of these facilities can lead to cracking and subsequent equipment failure. Corrosion of iron in steel requires the presence of water and aqueous species that can be reduced while the iron is oxidized. The presence of oxygen, acid gases like CO<sub>2</sub>, H<sub>2</sub>S and other natural organic acids contained in the produced fluids also contribute to corrosion of oil and gas facilities.

There are different categories of corrosion inhibitors such as passivating (anodic), Cathodic, Vapour-phase or volatile, Film-forming. Film-forming corrosion inhibitors are generally used for protection and fortification of oil, condensate and gas production lines. Application of passivating corrosion inhibitors are rare in oil and gas production. They are mostly used in low-salinity applications such as utility systems. When a passivating inhibitor is used, an unreactive thin surface is formed on the metal which stops access of corrosive substances to the metal, thereby inhibiting further corrosion. Examples of passivating corrosion inhibitors are: phosphates and polyphosphates, tungsten, silicates, chromates, meta-, ortho-, and pyrovanadates (NaVO<sub>3</sub>, Na<sub>3</sub>VO<sub>4</sub> and Na<sub>4</sub>V<sub>2</sub>O<sub>7</sub> respectively ) etc. several of the passivating inhibitors are metal anionic species.

Phosphate corrosion inhibitors help maintain a mineral passivation layer on the inside of steel pipes, protecting them from corrosion with little corrosion, chlorine disinfectant levels remain stable. See plate 2.

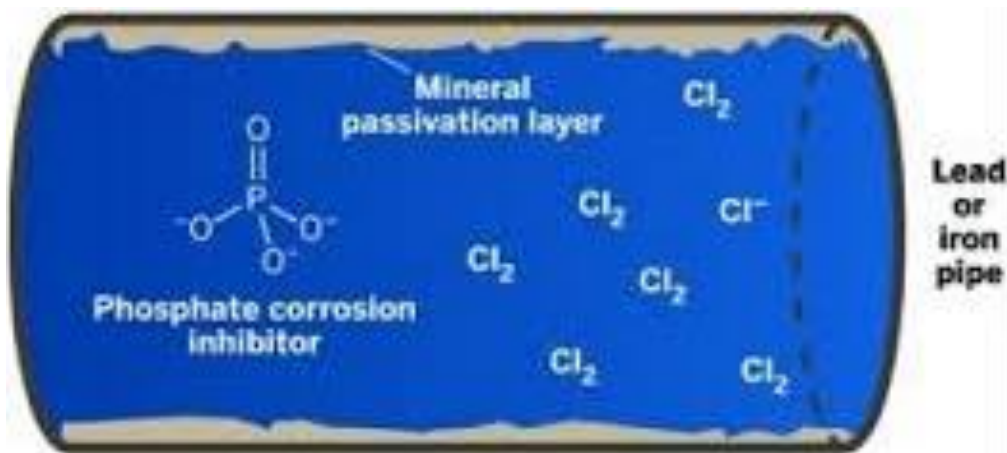


Plate 2. Phosphate corrosion inhibitors in pipes

Cathodic inhibitors either slow the cathodic reactions itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species. They are not used in production operations but have been used in drilling fluids. An example of cathodic corrosion inhibitors is zinc oxide which works by retarding corrosion by inhibiting the reduction of water to hydrogen gas. Corrosion inhibitors are typically a blend of components like:

Phosphate Esters, Sulphur Compounds, Various Nitrogenous Compounds, Quaternary ammonium salts and betains, Amidoamines and Imidazolines, Polyhydroxy and ethoxylated amines/amidoamines, Amides other heterocyclic.

#### Chemistry of Cathodic Inhibitors

- (i) Inhibition of oxygen absorption and hydroxyl ions



The formation of  $\text{OH}^-$  ions can be prevented either by removing  $\text{O}_2$  from the medium or by decreasing the diffusion of  $\text{O}_2$  in the cathode.  $\text{O}_2$  is removed either by adding reducing agents like  $\text{Na}_2\text{SO}_3$ ,  $\text{N}_2\text{H}_4$ , etc



Salts of Zn, Mg or Ni are added to corroding medium to reduce the diffusion of  $\text{O}_2$  towards cathode. These salts react with  $\text{OH}^-$  ions at the cathode forming insoluble hydroxides which are adsorbed at the cathode.

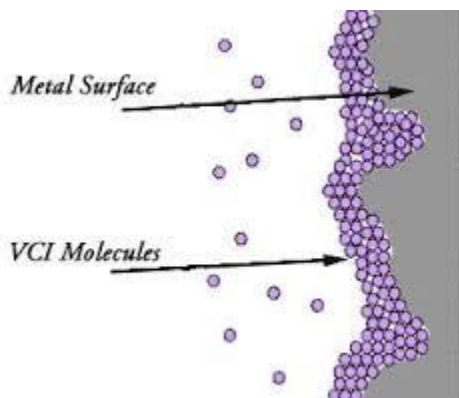


Plate 3. Migrating corrosion inhibitors and vapour-phase corrosion inhibitors

Vapour-phase corrosion inhibitors are organic compounds which adsorb onto surfaces of metals. Examples are diethylamine phosphate, trimethylamine, dicyclohexylamine carbonate, dicyclohexylamine nitrite etc. Plate 3 shows migrating corrosion inhibitors and vapour-phase corrosion inhibitors.

Hydrogen sulphide and carbondioxide corrosion are better prevented by film-forming corrosion inhibitors. The mode of operation is by adsorbing on the surface of the metal thereby forming a protective layer that physically prevents corrosive chemicals from penetrating to the metal surface. They are mostly organic amphiphiles i.e. surfactants that have a polar head group and a hydrophilic tail (plate 4).

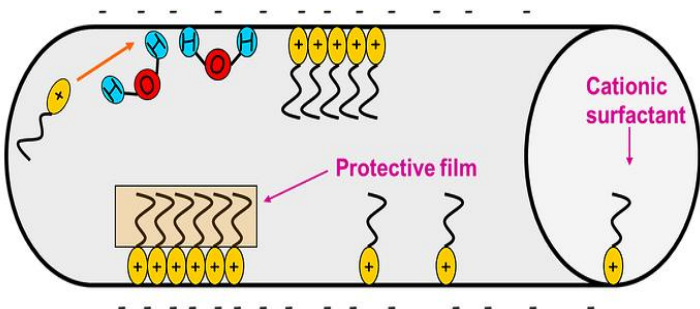
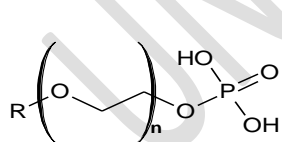
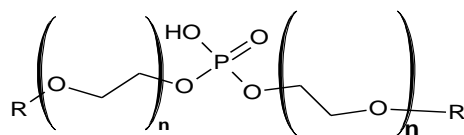


Plate 4. Surfactants with polar head and hydrophilic tail

The most common categories of surfactants used as film-forming corrosion inhibitors are phosphate esters, various nitrogenous compounds like amine salts of carboxylic acids, polyhydroxy and ethoxylated amine/amidoamines, amides etc; and sulphur compounds with heteroatoms such as nitrogen. Biodegradable polyaminoacids have also been employed in environmentally sensitive areas. Typical phosphate ester film-forming corrosion inhibitors:

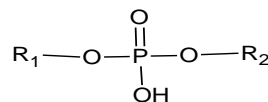


Phosphate monoesters



phosphate esters

P<sub>2</sub>O<sub>5</sub> based



mixed phosphate diesters



## Figure 6. Corrosion and Scale Inhibitors

The two most expensive problems in the petroleum industries are corrosion and scale deposition. This is because most of surfaces and equipment used in production, transport and refining operations are corrodible. Oil field corrosion is associated with deposition conditions and contact with oxygen. Iron sulphide or other solid particles can deposit on the metal surface and prevent access by corrosion inhibitors. Corrosion inhibitors can be generally classified into the groups:

- (i) Amides and imidazolines
- (ii) Salts of nitrogenous molecules with carboxylic acids, i.e., fatty acids and naphthenic acids
- (iii) Nitrogen quaternaries
- (iv) Polyoxylated amines, amides, imidazolines, and
- (v) Nitrogen heterocyclics.

The use of stainless steels have been used efficiently to combat hydrogen sulphide ( $H_2S$ ) and carbon dioxide ( $CO_2$ ) corrosion, but these materials are susceptible to hydrochloric acid ( $HCl$ ).  $HCl$  is used in oil and gas production to stimulate the formation. Epoxide resins with aromatic amines are used as coatings for internal corrosion of petroleum pipelines [28, 29]. Chemicals employed as downhole corrosion inhibitors are polymers with high amine content like polybutadiene. Also downhole metal surfaces in oil and gas wells are inhibited from corrosion with a combination of vinyl monomer such as an unsaturated acid, acrylonitrile, vinyl ester or N-vinyl-2-pyrrolidone and mercaptan Figure 7.

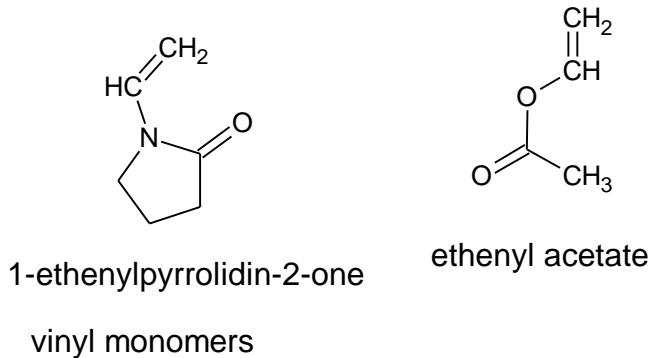


Figure 7. Relevant vinyl monomers

### 1.10 Scale Inhibitors and Removal by Acid treatment

In the petroleum industries, activities such as production and transport are usually faced with deposition of scales. This often occurs when there a change in temperature during injection operations and the solution becomes supersaturated. A mixture of two chemicals which easily precipitates usually leads to scale formation. A typical example is a mixture of hydrogen fluoride with a solution containing calcium ions. Scales may contain calcium carbonate, barium sulphate, gypsum, strontium sulphate, iron carbonate, iron oxides, iron sulphides, and magnesium salts. When a substance that react with probable Scale-forming substances is added stop or to subdue crystal formation it can lead to Inhibition of Scales. Scale formation is the deposition of sparingly soluble inorganic salts from aqueous solutions. In addition, there is another type of scale containing metal ions in which the anions are organic carboxylates or naphthenates. When scales are formed, they block pore throats in the near-wellbore region or in the well causing formation damage and loss of productivity. Scales forms along the production pipe casing a

reduction in the internal diameter thereby blocking flow; scales can also form in processing facilities.

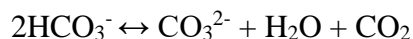
Scale inhibitors are generally categorized as organic or inorganic. Examples of inorganic scale inhibitors are condensed phosphate, such as polymetaphosphates or phosphate salts. Organic scale inhibitors includes polyacrylic acid (PAA), phosphinocarboxylic acid, sulfonated polymers, and phosphonates. The phosphonates are good at high temperatures, while the sulfonated polymers perform better at low temperatures [30, 31]. Most scale removers or inhibitors such as acids which are introduced downhole to remove scales are corrosive to the production tubing and casing liners. The addition of Inhibitors to the stimulation fluids minimizes the corrosion of tubing and casing liners.

### **Types of scales:**

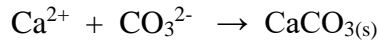
There are different scales encountered in the oil and gas industry. They include

- Calcium carbonate
- Sulphate salts of calcium, strontium and barium
- Sulphide scales – iron (II), zinc, and lead (II) salts
- Sodium chloride

Calcium carbonate scale: Although calcium bicarbonate is water soluble, calcium carbonate is not. Formation water usually contains bicarbonate ions as well as calcium ions. Calcium carbonate can deposit.

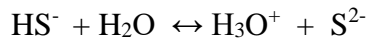
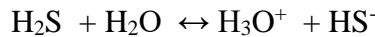


If pressure drops, the equilibrium moves to the right with more CO<sub>2</sub> forming. As a result, more carbonate ions are formed. At some point, the concentration of carbonate ions may be high enough that calcium carbonate precipitates.



Sulphate scales are usually formed when formation water and injected seawater mix. Also, two different non-scaling well fluids may mix in topside flow lines and cause topside scale problem.

Scale formed from sulphide compounds are less common than carbonate and sulphate scales but are still a major challenge in the oil and gas industry if not controlled. Some hydrogen sulphide is present in formation waters. For oil wells, the bulk of this comes from the activity of sulphate-reducing bacteria (SRBs) on the sulphate ions in the injected seawater.



Formation water may sometimes be saturated with sodium chloride. As the temperature of produced water decreases, sodium chloride may precipitate out. Water flash-off into the gas phase as pressure decreases during production will concentrate solutions of sodium chloride, which may eventually also lead to halite (sodium chloride) precipitation. Scales can also be layered and of mixed composition, for example, containing both carbonate and sulphate scales, at the appropriate field conditions. Formation water generally comprises of calcium carbonate which is insoluble and calcium bicarbonate which is soluble. Both are present in their ionic forms. Plate 5 shows examples of scales.



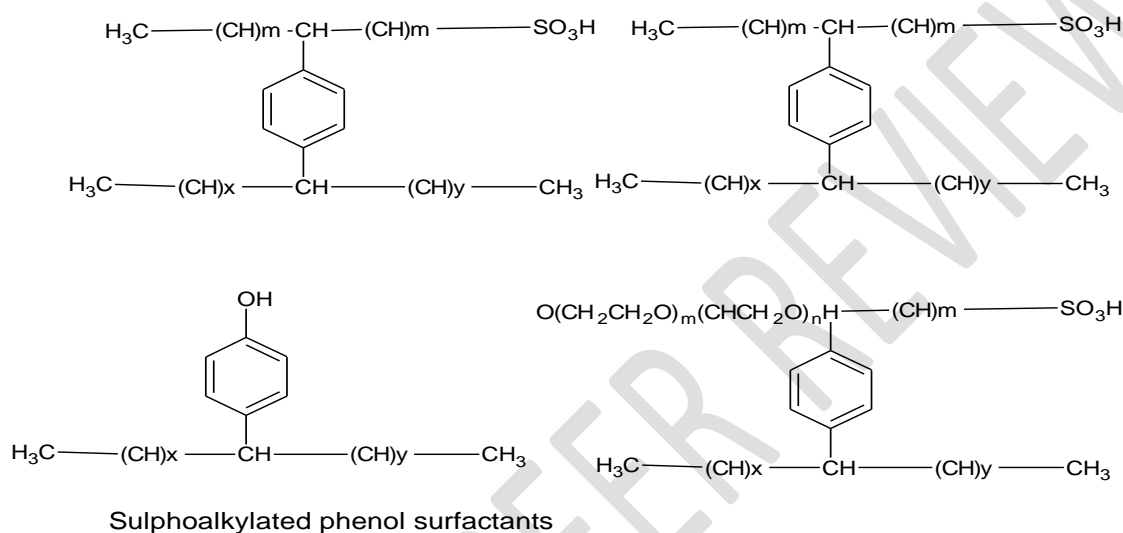
Plate 5 Scales

## 2.0 Enhanced Oil Recovery

The conventional crude oil production method can recover 30 – 40% of oil reserves. Enhanced Oil Recovery (EOR) is used to recover the rest of the crude oils from the reservoir. The methods used in Enhanced oil recovery involves the use of chemical and gas floods, steam, combustion, and electric heating.

Chemical floods involves the injection of definite chemicals which include polymers, surfactants, and alkalis, most of these chemicals are often combined.

Alkyl-aryl sulfonates have been known as good for EOR by surfactant flooding but for waxy crudes, the use of olefins greater than C<sub>10</sub> are used for the alkylation of xylene sulfonate or toluene sulfonate, in contrast to conventionally used alkyl-aryl sulfonates, which generally have a narrow range of olefin carbon number, such as C<sub>12</sub>-xylene sulfonate [32]. Some examples of olefinic sulphonic acid surfactant (linear or branched) are shown in figure 8



Figures 8. Chemical structure of sulphonalkylated phenol surfactants

Field trials revealed that the injection of silicone on a gas production was beneficial and the gas production tripled and was sustained for at least six months [33].

Hydrochloric acid (6 –30%.) is frequently used, sometimes also with hydrofluoric acid and sometimes surfactants like isononyl phenol added [34]. The environment is then made acidic thus converting the sulfonates into sulfonic acid, which has a lower interfacial tension (IFT) toward oil, thus having a better efficiency in forcing out oil compared with the neutral, aqueous solutions of sulfonates. Cyclic injection can be applied and sulfuric acid has also been used for acid treatment. Injecting additional aqueous liginosulfonate increases the efficiency of a sulfuric

acid treatment. A combination of Hydrochloric acid with chlorine dioxide can be used as a treatment fluid in water injection wells that get impaired by the deposition of solid residues [35, 36].

## 2.1 Demulsifiers

Emulsions are colloidal dispersion, droplets of one phase dispersed in a second phase. Crude oil is almost always produced as a water-in-oil emulsion, i.e. water droplets stabilized in a continuous crude oil phase plate 6 is representation of types emulsion. . Free produced water may also be present depending on the water cut. The water and dissolved salts in the emulsion must be separated out before the oil is accepted for export, further transportation or treatment at the refinery. This process is called demulsification or dehydration. There is a specified maximum value of water content in crude before it is sold. characteristically, the desired maximum water content is in the range of 0.2-0.5%. the water separated from the water-in-oil emulsion usually contain dispersed oil as an oil-in-water emulsion. This also need treatment called de-oiling.

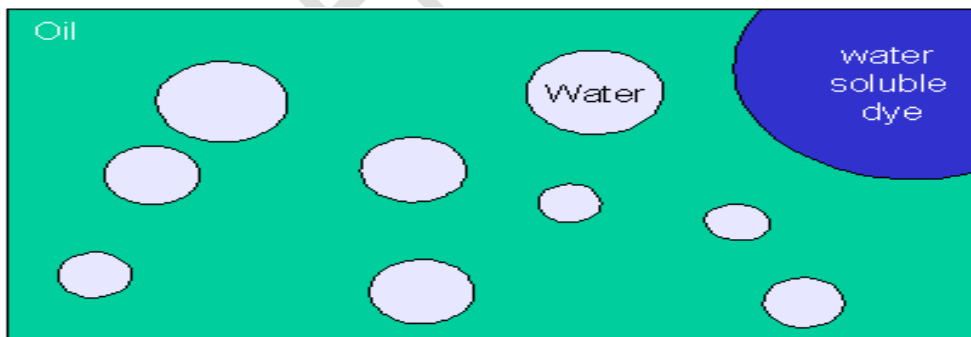




Plate 6 Representation of types emulsion

Emulsions are formed due to turbulence in the production tubing and pipeline when passing through chokes as the wellhead. Demulsifiers are added to resolve the problem of emulsions usually encountered in the oil and gas industries. Depending on the water phase, the concentration of the added demulsifier is in the range of 5-500 ppm. Sufficient mixing is required to get the demulsifier to the oil-water interface. In addition, time must be allowed for the coalesced droplets to phase separate. Any emulsion that is not broken is known as slop. A prerequisite for good demulsification is that the oil-water emulsion should be free of gas. If the crude oil contains significant amount of gas, the formation of gas bubbles will cause unnecessary agitation restricting the ability of the chemical demulsifier to produce a clean interface. Gas may be beneficially removed upstream in a gas separator.

On breaking the emulsion, the bulk of the water would be separated and the oil ready for further transportation and processing at the refinery. Residual oil is still contained in the water separated out at the processing facilities in the form of an oil-in-water emulsion or reverse emulsion. The oil can be separated from the water using water clarifiers, de-oilers or reverse emulsion breakers.

The existence of water-in-oil emulsions usually causes corrosion and the growth of microbes in the water-moistened parts of the pipelines and storage tanks.



Prior to refining operation, crude oils are usually desalted by emulsification with fresh water, followed by demulsification. This is because Crude oils with high salt contents might lead to breakdown and corrosion during refining, and an emulsion breaker, or demulsifier, is used to break the emulsion at the lowest possible concentration, to completely separate the water and decrease the salt content to a lowest concentration.

In crude oil production, demulsifiers are usually injected at the processing facilities before the separator. Emulsions that are slowly resolved need adequate time to separate. The fluids are hotter upstream, thus will result in faster emulsion resolution. Often, a range of demulsifiers and blends are taken to the process plants and tested by trial and error. Oils with a high viscosity hold up more and larger water droplets. Lowering the viscosity increases both the rate at which droplets settle and the mobility of water droplets, the speed at which they coalesce and separate out.

Over the years, oilfield chemical manufacturers have developed an ever-increasing range of products in attempts to destabilize emulsions. Water-in-oil demulsifiers are polymeric non-ionic chemicals with molecular weight of about 2,000-50,000. Anionic and cationic polymers can be used depending on the emulsion-stabilizing chemicals in the feed-stream or wetting agents. Examples of water-in-oil demulsifiers are polyalkoxylates of polyols, polyurethanes, vinyl polymers, polysilicones, ester derivatives, alkylphenol-aldehyde resin alkoxylates etc. blends of a demulsifier and a polyalkylene glycol ether have been claimed to give better emulsion breaking. Most classes of water-in-oil demulsifiers are oil-soluble and are deployed as solutions in hydrocarbon solvents. Also, mixed aromatic/low alcohol solvents are commonly used. From the above listed examples, many categories of demulsifiers contain polyalkoxylate chains.

The Polyalkoxylates can be produced by ring-opening of the oxides of ethylene, propylene, butylene or tetrahydrofuran using a base an amine or alcohol. Polyoxyethylene chains are very hydrophilic, polypropylene oxide chains are mildly hydrophobic while polybutylene chains are very hydrophobic. Thus, one can make a range of products using the same alcohol or amine base with varying side chains. A number of polyalkyleneamines are obtainable commercially. They can be derivatized with several quantities of ethylene oxide and propylene oxide to produce branched demulsifiers. Examples of polyethyleneamines are ethyleneamine (EDA), diethylenetriamine (DETA), triethylenetriamine (TETA) and higher polyethyleneamines. Studies on DETA-based demulsifiers showed that roughly equal amounts of Ethylene oxide and propylene oxides in the side chains gave optimum performance

Products based on ring-opening reactions of epoxydized fatty acid esters with amines, diamines or polyamines after subsequent alkoxylation have shown to have excellent breaking effect even at low concentrations. Figure 9. shows the structure of Diethylenetriamine Demulsifiers which contain amide groups can be produced by reacting DETA with fatty acids (adipic acid) followed by alkoxylation.

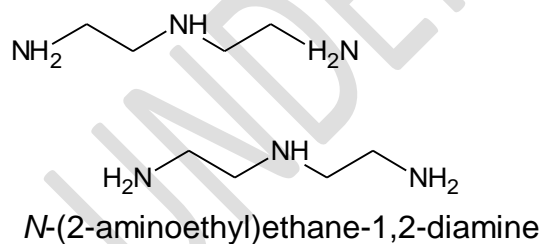
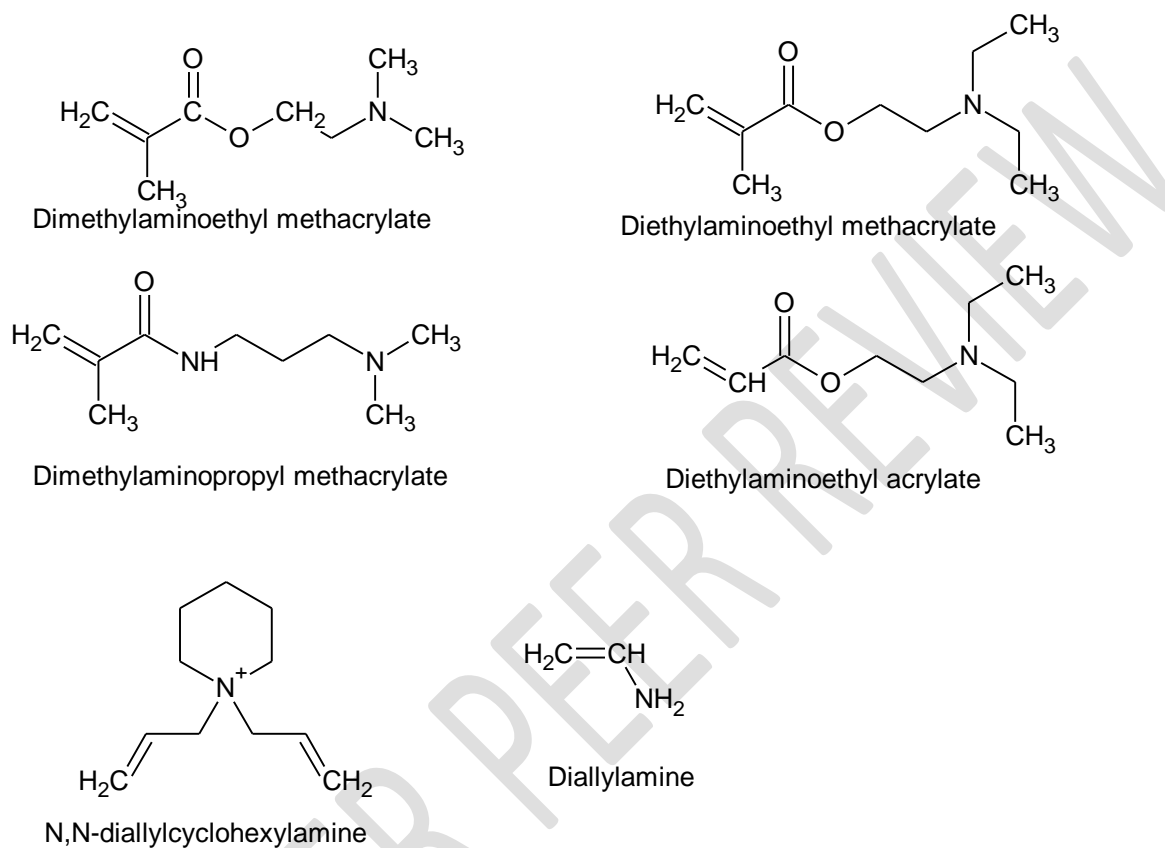


Figure 9. Structure of Diethylenetriamine (DETA)

Some demulsifiers can also have secondary function. A typical example is the salt of an alkyl sulphonic acid and an alkylamine which is an efficient demulsifier but then possesses corrosion inhibiting properties. Figure 10 shows methacrylic monomers used as demulsifer.



### Methacrylic monomers for demusifiers

Figure 10. Structures of Methacrylic monomers

### 2.3 Oil Spill Treating Chemicals

There are numerous chemicals used in treating oil spills. They are grouped into the following categories: (i) solidifiers (ii) demulsifying agents (iii) surface-washing agents and (iv)

dispersants. These chemicals should possess characteristics such as a long shelf life, environmentally friendly, non-toxic, non-polluting, biodegradable, highly active and noncorrosive. Chemicals such as an oil-soluble, oxyethylated alkyl phenol, an alkyl phosphate of a higher fatty acid alcohol, and a fatty acid amide of diethanol amine, are suitable for removing crude oils and petroleum products from water surfaces [37]. Copolymers of dienes and p-alkylstyrenes are used as dispersants. Corexit 9580 is a mixture of a sorbitan monoester of an aliphatic monocarboxylic acid, a polyoxyethylene adduct of a sorbitan monoester, a water-dispersible salt of a dialkyl sulfosuccinate, a polyoxyethylene adduct of a sorbitan triester or a sorbitol hexaester of an aliphatic monocarboxylic acid, and propylene glycol ether as solvent [38]. It shows little fish toxicity, low dispersiveness, and effective rock cleaning capability.

### **3.0 Considerations For Application of Oilfield Chemicals**

Oilfield chemicals are generally used in operational processes of the oil and gas industry to achieve specific purposes. These functions can be broadly categorized into three (i) Integrity management (ii) Flow assurance and (iii) Process optimization.

(i) Integrity management of oil and gas facilities: The major purpose of applying oilfield chemicals is to prevent all forms of corrosion. This in turn safeguards the facilities to avert failure during exploration, production and processing of crude oil and natural gas. Facilities concerned are well tubing, pipes and pipelines, storage tanks, separators etc. The class of oilfield chemicals employed to maintain integrity of these facilities include corrosion inhibitors, oxygen scavengers, hydrogen sulphide scavengers, sand control chemicals and biocides.

(ii) Flow assurance: This refers to designs, strategies and principles ensuring successful and economical flow of hydrocarbon stream from reservoir to the point of sale i.e. ensure unrestricted flow of process fluids. Examples of oilfield chemicals employed in oil and gas operations to obtain maximum flow assurance are Scale Inhibitors, hydrate inhibitors, wax inhibitors, asphaltene inhibitors, naphthenate inhibitor and acid stimulation.

(iii) Process optimization: This refers to the discipline of process adjustment to optimize some specific set of parameters without violating some constraint. It is commonly done to minimize cost, maximize throughput and ensure efficiency of process operations. Examples of oilfield chemicals to fit into this category are demulsifiers, water clarifiers, defoamers, drag reducers etc. Water Clarifiers which are also known as De-oilers are applied after demulsifiers and subsequent separation, clean up water before discharging to sea or other water bodies.

**Environmental Restrictions:** Both the developed and developing nations of the world have guidelines, protocols and regulations on the classification of chemicals based on the hazards and risks they portend on the users as it relates to health and safety. Operators in the oil and gas industries should consider environmental impact of the chemicals. These indispensable and vital information are contained in the Material safety Data Sheets (MSDS) for the chemical which must accompany shipment of all potentially hazardous products according to laid down laws and regulations. In general, it is noted that the UK and US are strict while the Africa and other third world countries are not so strict with environmental regulations.

#### 4.0 CONCLUSION

The energy landscape is changing worldwide. Consequently to deliver global demand for energy, operators of the oil and gas industry has put unparalleled programmes of different extraction methods in the search for and development of old and new hydrocarbon reserves. Activities such as enhanced oil recovery, drilling of complex deepwater wells, hydraulic fracturing exploiting resources and innovative technologies which employ the use of oilfield chemicals have resulted in economical sustainability of crude oil and natural gas. The oil and gas process plant is incomplete without the use of chemicals in its operations. Varying problems are encountered during exploration, production and processing activities. Oilfield chemicals are produced to surmount, minimize and reduced to barest minimum most of the challenges encountered during oil and gas operations. The use of oilfield chemicals in exploration, production and processing of crude oil and natural gas is vital to operating at lower costs, obtaining maximum efficiency, process optimization and enhanced productivity in the oil and gas industry.

## REFERENCES

1. Johannes KF. Petroleum engineer's guide to oil field chemicals and fluids, 2012.
2. Brazzel RL. Multi-component drilling fluid additive, and drilling fluid system incorporating the additive. US Patent 7 635 667, assigned to Ambar Lonestar Fluid Services, LLC (Lafayette, LA), December 22, 2009.
3. Melbouci M, Sau AC. Water-based drilling fluids. US Patent 7 384 892, assigned to Hercules Incorporated (Wilmington, DE), June 10, 2008.
4. Ravi KM, Whitfill DL, Reddy BR. Methods of drilling wellbores using variable density fluids comprising coated elastic particles. US Patent 7 482 309, assigned to Halliburton Energy, 2009.
5. Patel BB, Muller GT. Compositions comprising an acrylamide-containing polymer and process therewith. EP Patent 728 826, assigned to Phillips Petroleum Co., August 28, 1996.
6. Ashjian H, Peel LC, Sheerin TJ, Williamson RS. Non-toxic biodegradable well fluids. WO Patent 9 509 215, assigned to Mobil Oil Corp., April 06, 1995.
7. Jones CK, Acker DB. Oil-based drilling muds with increased viscosity. EP Patent 922 743, assigned to Nalco Exxon Energy Chem. L, June 16, 1999.
8. Rastegaev BA, Andreson BA, Raizberg YL. Bactericidal protection of chemical agents from biodegradation while drilling deep wells. *Stroit Neft Gaz Skvazhin Sushe More*, 1999; (7–8), 32–34.
9. Sikora, D., 1994. Hydrazine – a universal oxygen scavenger (hydrazyna – niwersalny inhibitor korozji tlenowej w pluczkach wiertniczych). *Nafta Gaz (Pol)* 50 (4), 161–168.
10. Kondo, M., Sawada, T., 1996. Readily dispersible bentonite. US Patent 5 491 248, assigned to Hojun Kogyo Co. Ltd., February 13, 1996.
11. Fabrichnaya, A.L., Shamraj, Y.V., Shakirzyanov, R.G., Sadriev, Z.K., Koshelev, V.N., Vakhrushev, L.P., Tavrín, A.E., 1997. Additive for drilling solutions with high foam extinguishing properties – containing specified surfactant in hydrocarbon solvent with methyl-diethyl-alkoxymethyl ammonium methyl sulphate. RU Patent 2 091 420, assigned to Etn Co. Ltd., September 27, 1997.

12. Nicora, L.F., McGregor, W. M. Biodegradable surfactants for cosmetics find application in drilling fluids. In: Proceedings Volume, IADC/SPE Drilling Conf. (Dallas, 3/3–6/98), 1998, pp. 723–730.
13. Grey, R. A. Process for preparing alternating copolymers of olefinically unsaturated sulfonate salts and unsaturated dicarboxylic acid anhydrides. US Patent 5 210 163, assigned to Arco Chemical Technol. Inc., May 11, 1993.
14. Peiffer, D. G., Bock, J., Elward-Berry, J. Thermally stable hydrophobically associating rheological control additives for water-based drilling fluids. CA Patent 2 055 011, assigned to Exxon Research & Eng. Co., May 07, 1993.
15. Burrafato, G., Carminati, S., 1994. Aqueous drilling muds fluidified by means of zirconium and aluminium complexes. EP Patent 623 663, assigned to Eniricerche SPA and Agip SPA, November 09, 1994.
16. Dolganskaya, S.I., Sharipov, A.U. Removal from hole of junk and stuck drilling equipment –by dissolving latter with mixture of nitric and hydrochloric acids with added sodium nitrate and ethanolamine. SU Patent 1 782 271, assigned to W Sibe Deep Pros Dril Des., December 15, 1992.
17. Dealy, S. T., Chatterji, J. Chemical wash compositions for removing drilling fluids. US Patent 7 662 752, assigned to Halliburton Energy Services, Inc. (Duncan, OK), February 16, 2010.
18. Walele, I. I., Syed, S. A. Process for making *N*-acyl taurides. US Patent 5 434 276, assigned to Finetex, Inc. (Elmwood Park, NJ), July 18, 1995.
19. Bromley, M. J., Gaffney, S. H., Jackson, G. E. Oilfield emulsion control, techniques and chemicals used to separate oil and water. In: Proceedings Volume, Volume 3, Inst. Corrosion UK orrosion 91 Conf., Manchester, UK, October 22–24, 1991.
20. Dahlmann, U., Feustel, M. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. US Patent 7 341 617, assigned to Clariant Produkte (Deutschland) GmbH Sulzbach, DE, March 11, 2008.
21. Kannan, K., Punase, A. Low-dosage, high-efficiency, and environment-friendly inhibitors: a new horizon in gas hydrates mitigation in production systems. In: SPE International Symposium on Oilfield Chemistry, 20–22 April 2009, no. 120905-MS, SPE, Society of Petroleum Engineers, The Woodlands. Texas, pp. 1–8.



22. Rose, G.D., Tetot, A.S., Doty, P. A. Process for reversible thickening of a liquid. GB Patent 2 191 716, December 23, 1987.
23. Gerez, J.M., Pick, A. R. Heavy oil transportation by pipeline. In: Proceedings Volume, Volume 2 1st Asme et al Int. Pipeline Conf., Calgary, Can, June 9–13, 1996, pp. 699–710.
24. Padron, A. Stable emulsion of viscous crude hydrocarbon in aqueous buffer solution and method for forming and transporting same. EP Patent 672 860, assigned to Maraven SA, September 20, 1995.
25. Rivas, H., Acevedo, S., Gutierrez, X. Emulsion of viscous hydrocarbon in aqueous buffer solution and method for preparing same. GB Patent 2 274 254, assigned to Intevep, July 20, 1994.
26. Rodriguez, D., Quintero, L., Terrer, M.T., Jimenez, G.E., Silva, F., Salazar, P. J. Hydrocarbon dispersions in water. GB Patent 2 231 284, November 14, 1990.
27. Gregoli, A.A., Olah, A. M. Low-temperature pipeline emulsion transportation enhancement. US Patent 5 156 652, assigned to Canadian Occident Petrol. Ltd., October 20, 1992.
28. Camberlin, Y., Grenier, J., Poncet, S., Bonnet, A., Pascault, J.P., Sautereau, H. Utilization of polymer compositions for the coating of surfaces, and surface coating containing such compositions (utilisation de compositions de polymeres pour le revetement de surfaces et revetement de surfaces comprenant ces compositions). EP Patent 931 819, assigned to Inst. Francais Du Petrole, July 28 1999.
29. Petersen, H., Martens, J., Harms, W., Kramer, U. Process for avoiding the formation of condensates, hydrates or ice in the decompression of natural gas stored in salt caverns (verfahren zur vermeidung der bildung von kondensaten, hydraten oder eis bei der entspannung von in salzkavernen gespeichertem erdgas). DE Patent 3 927 905, assigned to Energieversor Weser Ems A, February 21, 1991.
30. Talbot, R.E., Jones, C.R., Hills, E.. Scale inhibition in water systems. US Patent 7 572 381, assigned to Rhodia UK Limited, Hertfordshire, GB, August 11, 2009.
31. Vilorio, A., Castillo, L., Garcia, J.A., Biomorgi, J. Aloe derived scale inhibitor. US Patent 7 645 722, assigned to Intevep, S.A., Caracas, VE, January 12, 2010.
32. Lakatos, I., Tóth, J., Lakatos-Szabó, J., Kosztin, B., Palásthy, G., H. Woltje,. Application of silicone microemulsion for restriction of water production in gas wells. In:

Proceedings Volume, SPE 13th European Petroleum Conference, Aberdeen, Scotland, U.K., October 29–31, 2002.

33. Gorodnov, V. P., Ryskin, A.Y., Pavlov, M. V. Increasing oil extraction from stratum – by pumping- in hydrochloric acid solution or its mixture with hydrofluoric acid or ammonium fluoride, followed by pumping aqueous solution or surfactant. SU Patent 1 795 092, assigned to Giprovostokneft Des. Inst., February 15, 1993.
34. Abdulmazitov, R.G., Muslimov, R.K., Zakirov, A. F., Khajretdinov, F. M. Oil recovery from carbonate oil-bearing seam – involves cyclic injection of acid solutions of increasing concentrations after reduction of seam pressure. RU Patent 2 073 791, assigned to Tartar Oil Inst., February 20, 1997.
35. Cavallaro, A., Curci, E., Galliano, G., Vicente, M., Crosta, D., Leanza, H. Design of an acid stimulation system with chlorine dioxide for the treatment of water-injection wells. In:Proceedings Volume, 7th SPE Latin Amer. & Caribbean Petrol. Eng. Conference, Buenos Aires, Argentina, March 25–28, 2001.
36. Braden, M.L., Allenson, S. J. Method for separating liquid from water using amine containing polymers. US Patent 5 021 167, assigned to Nalco Chemical Co., June 4, 1991.
37. Chaplanov, P.E., Chernikov, A.D., Mironov, O.G., Semanov, G.N., Svinukhov, A.G., Yaremenko,A.G., et al., Removing oils and petroleum products from water surfaces – using mixture of oxyethylated alkyl- phenol, alkyl-phosphate and fatty acid diethanolamine. SU Patent 1 325816, October 15, 1992.
38. Canevari, G.P., Fiocco, R.J., Becker, K.W., Lessard, R. R. Chemical dispersant for oil spills.US Patent 5 618 468, April 08, 1997.