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 enormous 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 review 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 [1]. 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 strings and wellheads through the flowlines to the processing plant for 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 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 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. Table 1 is a summary of nnumerous oilfield chemicals used in the oil and gas industries and their functions.

Table 1. Some oilfield chemicals used in the oil and gas industries and their functions.

Oil Field Chemicals	**Functions**
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_2S gas, corrosion control
Oxygen scavengers	reduces oxygen levels, prevents oxygen 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 [2]. 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 [3, 4]. 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 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 (Na_2CO_3) are used due to the presence of Mg^{2+} and Ca^{2+} ions which causes hardness.

The ions are removed and precipitated as magnesium hydroxide ($Mg(OH)_2$ and calcium carbonate ($CaCO_3$).

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 [5].

Water-based muds (WBMs) have fundamental components such as polyacrylamide, carboxymethyl cellulose, acrylamide copolymer, polypropylene glycol (PPG) [6].

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 [7, 8].

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 [9]. Some of the structures of chemicals used for bacterial control (bactericides) or biocides recommended for drilling fluids are shown in Figure 1.

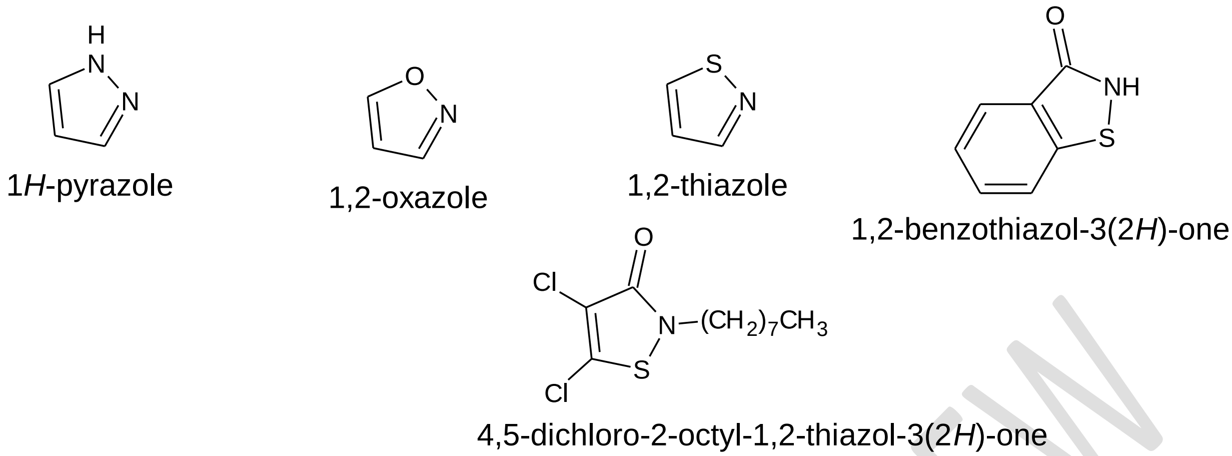


Figure 1. Structures of components of bactericides or biozides

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 [10].

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 [11].

1.4 Surfactants, Dispersants and Deflocculants

Surfactants (surface-active agent) are compounds that have 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. Others like alkylpolyglucosides (APGs) which are biodegradable can be added to polymer muds to reduce fluid loss, enhance rheology and temperature resistance [12, 13].

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 [14, 15, 16]. 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.

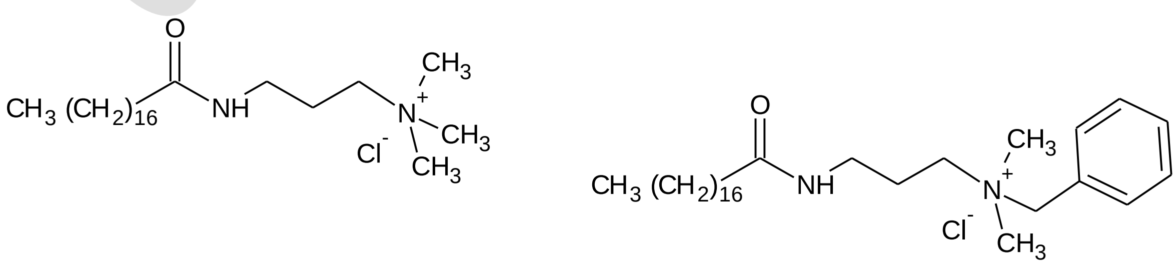


Figure 2 Quaternary ammonium surfactants

1.5 Cuttings, Junk and Filter Cake Removal

Chemicals like barium sulphate are ground, filtered and suspended in drilling fluid to remove cutting beds. Cutting beds are deposits of small size drill cuttings that build 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 cuttings beds from the borehole and transports them to the well surface. A mixture of nitric and hydrochloric acids 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 of 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 [16, 17].

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% [18]. 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 [19].

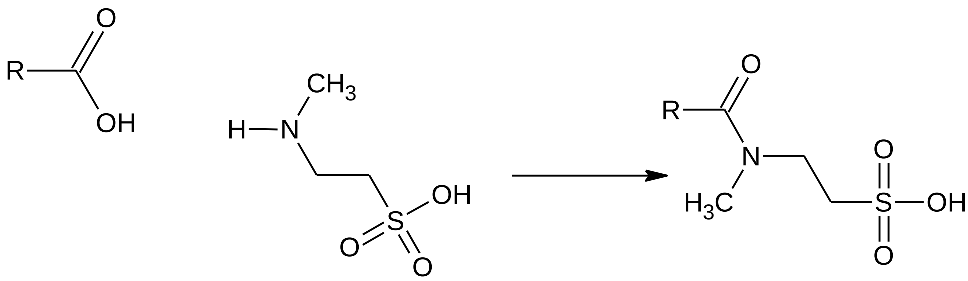


Figure 3. Acylation of N- Methyl-taurine.

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_2) and hydrogen sulphide (H_2S), water emulsified in the crude oil, naphthenic acids are the main cause of corrosion problems. They can also cause problems during refining, and processing [20]. Chemical additives are added to alleviate these problems. For example ammonia (NH_4), 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 [21].

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 [22].

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 butlymercaptans. The most important compounds are given in Figure 4.

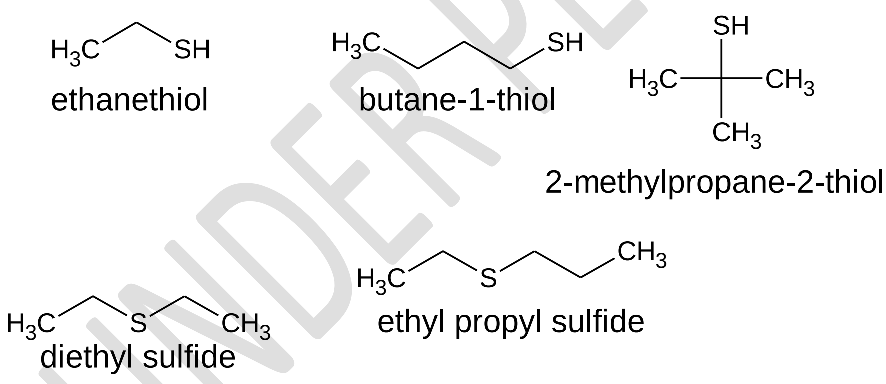


Figure 4. Structures of additives used for odorization

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 [23].

There are some parameters that should be taken 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 [24, 25]. 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 surfactant precursors. Aqueous buffer solution of sodium hydroxide with sodium bicarbonate or sodium is used for activation [25, 26]. During low temperature transportation, inorganic salts, such as aluminium nitrate can be used in small quantities (30 ppm) are additional stabilizers for the emulsion [27]. In addition to the surfactants used in low temperature transportation, chemicals such as salts, sugars and glycerol can be added as freezing point depressant [28].

1.7 Pour point depressants and chemical inhibition

The wax content of some crude oil is very high and it tends to pose problem during its transportation through pipelines especially in cold regions due to its 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 function of chemical inhibitors is that they are film formers which protect the pipeline surfaces. A few examples are shown the Figure 5

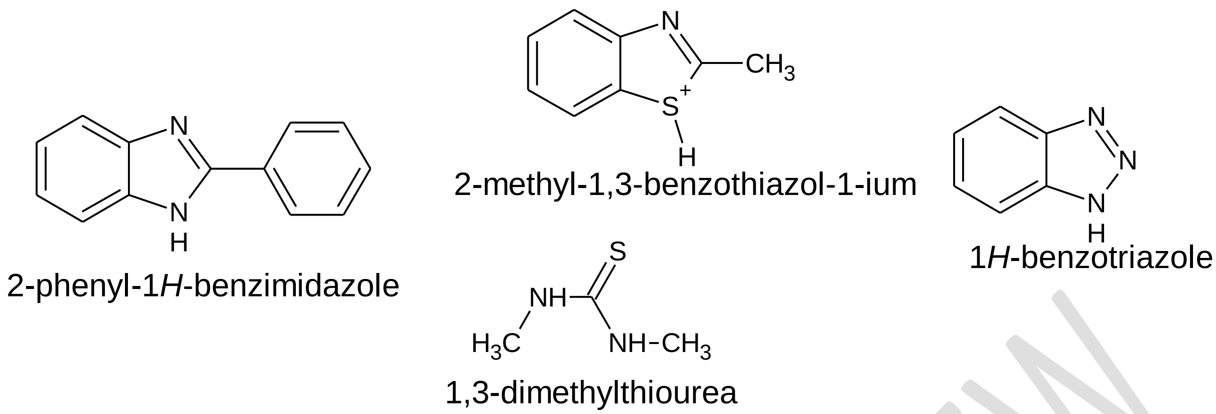


Figure 5. The structure of corrosion inhibitors used in oil production

1.8 Corrosion inhibitors

The deterioration of a substance, especially metals or their properties due to reaction or interaction with the environment is known as corrosion. Corrosion occurs in the oil and gas industry when steel comes in contact with an aqueous environment and rusts. In the oil and gas industry, carbon dioxide (CO_2) and hydrogen sulphide (H_2S) are commonly present, and water is their catalyst for corrosion [29].

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_2, H_2S 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 ($NaVO_3$, Na_3VO_4 and $Na_4V_2O_7$ respectively) etc. several of the passivating inhibitors are metal anionic species.

Phosphate corrosion inhibitors help maintain a mineral passivation layer inside the flint pipes, protecting them from corrosion while chlorine disinfectant levels remain stable, see plate 2.

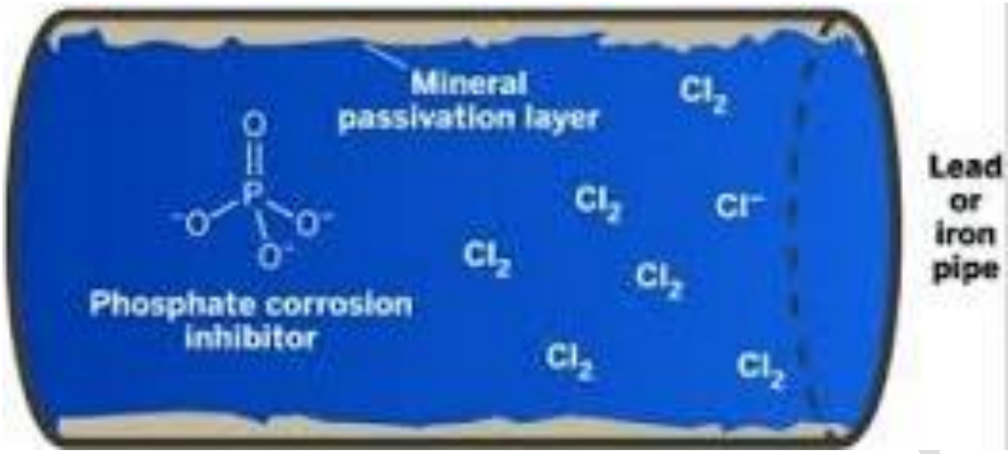


Plate 2. Phosphate corrosion inhibitors in pipes

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 such as:

phosphate esters, sulphur compounds, various nitrogenous compounds, quaternary ammonium salts and betains, amidoamines and imidazolines, polyhydroxy and ethoxylated amines/amidoamines, amides other heterocyclic.

There are different mechanisms that chemical inhibitors can stop wax deposition or gelling in pipelines. They can lower the WAT or pour point or can modify the wax crystals so as to prevent their cluster and deposition [30]. Chemicals that modify the WAT are known as wax inhibitors or wax crystal modifiers, while those that affect the pour point are known as pour point depressants (PPDs) or flow improvers [30]. Examples of low-cost wax dispersants include alkyl sulfonates, alkyl aryl sulfonates, fatty amine ethoxylates and other alkoxylated products, but these dispersants have shown limited effectiveness in the field when not blended with polymeric wax inhibitors [30].

1.8.1 Chemistry of cathodic inhibitors

(i) Inhibition of oxygen absorption and hydroxyl ions

$H_2O + ½O_2 + 2e^- \longrightarrow 2OH^-$ …………………………….equation 1

The formation of OH^- ions can be prevented either by removing O_2 from the medium or by decreasing the diffusion of O_2 in the cathode. O_2 is removed either by adding reducing agents such as Na_2SO_3, N_2H_4, etc

$O_2 + NH_2\text{-}NH_2 \longrightarrow N_2 + 2H_2O$…………………..equation 2

$2Na_2SO_4 + O_2 \longrightarrow 2Na_2SO_4$……………………………….equation 3

Salts of Zn, Mg or Ni are added to corroding media to reduce the diffusion of O_2 towards cathode. These salts react with OH^- ions at the cathode forming insoluble hydroxides which are adsorbed at the cathode.

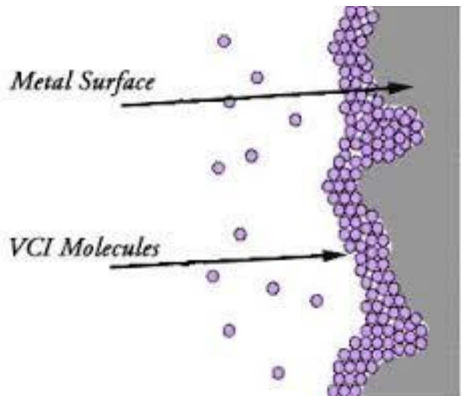


Plate 3. Migrating corrosion inhibitors and vapour-phase corrosion inhibitors

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).

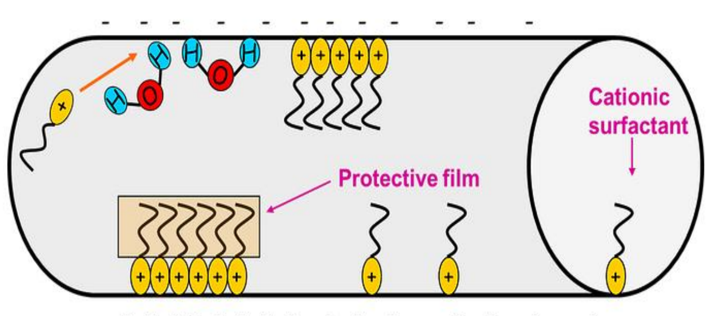


Plate 4. Adsorption of surfactants with polar heads and hydrophobic tails

The most common categories of surfactants used as film-forming corrosion inhibitors are phosphate esters, various nitrogenous compounds such as 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 are shown in Figure 6.

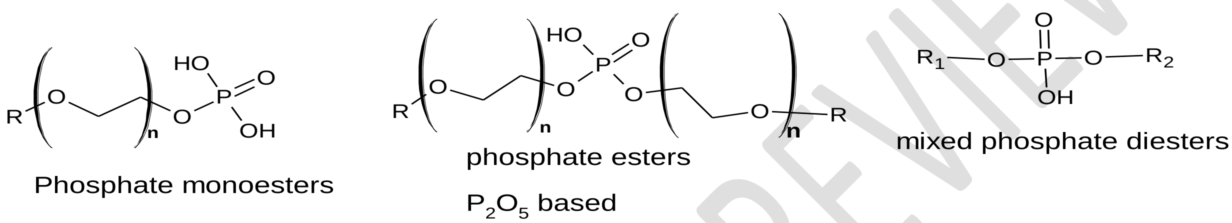


Figure 6. Corrosion and scale inhibitors

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

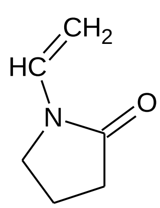
(ii) Salts of nitrogenous molecules with carboxylic acids, e.g, fatty acids and naphthenic acids

(iii) Nitrogen quaternaries

(iv) Polyoxylated amines, amides, imidazolines

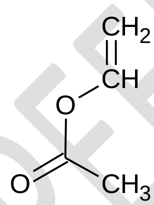
(v) Nitrogen heterocyclics.

The use of stainless steels has efficiently combated 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, 31]. Chemicals employed as downhole corrosion inhibitors are polymers with high amine content such as 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, vinylester or N-vinyl-2-pyrrolidone and mercaptan as depicted in Figure 7.



1-ethenylpyrrolidin-2-one

vinyl monomers



ethenyl acetate

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 reacts with probable scale-forming substance is added to stop or 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 [32, 33]. 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. There are different scales encountered in the oilfield. They include: Calcium carbonate, calcium sulphate, strontium and barium, sulphide scales (iron (II), zinc, and lead (II) salts), sodium chloride, iron, silicon sediment and other insoluble solids [34, 35].

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.

$2HCO_3^- \leftrightarrow CO_3^{2-} + H_2O + CO_2$ ………………………..equation 4

If pressure drops, the equilibrium moves to the right with more CO_2 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.

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$ ……………………....equation 5

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 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.

$H_2S + H_2O \leftrightarrow H_3O^+ + HS^-$ ……………………..equation 6

$HS^- + H_2O \leftrightarrow H_3O^+ + S^{2-}$ ………………………..equation 7

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, this will concentrate solutions of sodium chloride, which may eventually 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.

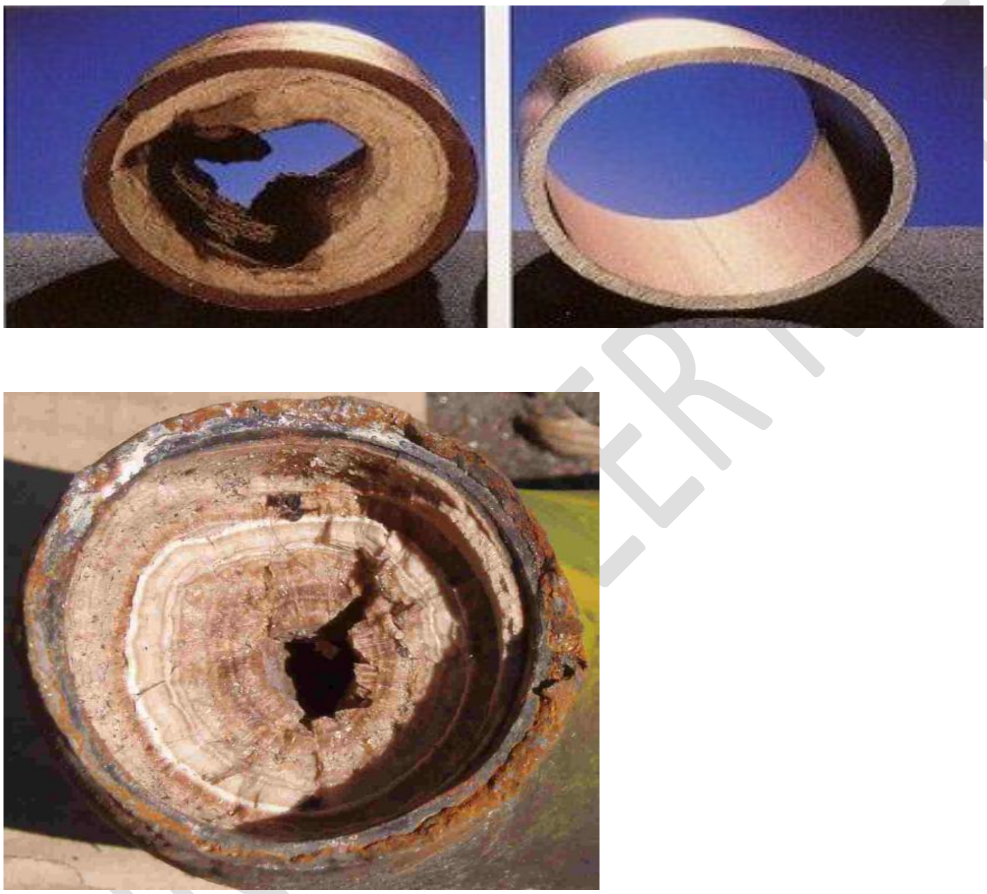


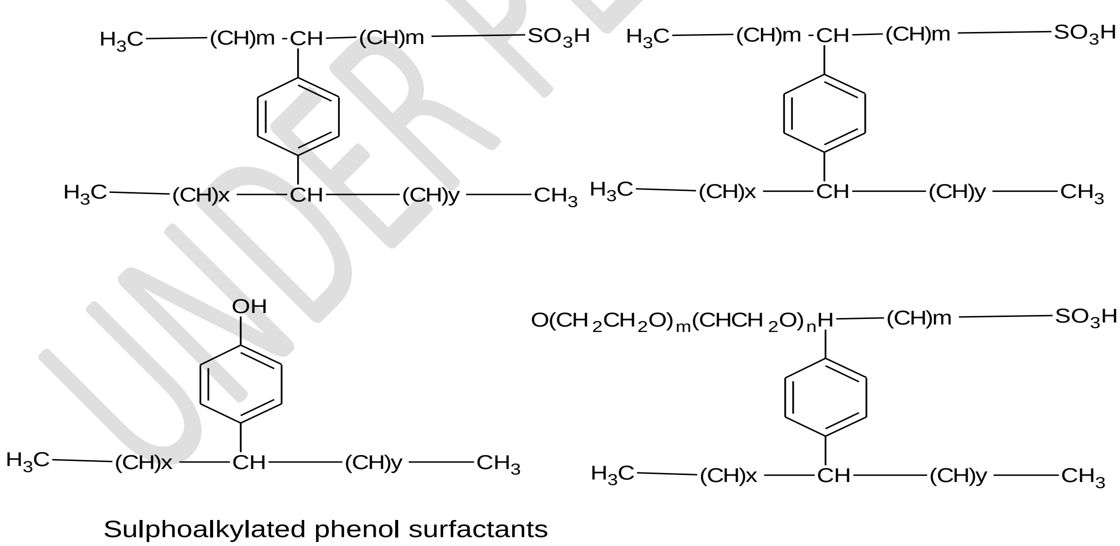
Plate 5. Scales formed in pipes

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. Olefins greater than C_{10} 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_{12}-xylene sulfonate [36]. 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 [37].

Hydrochloric acid (6 –30%,) is frequently used with hydrofluoric acid and sometimes surfactants like isononyl phenol added [38]. The environment is then made acidic thus converting the sulphonates into sulphonic 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 sulphuric acid has also been used for acid treatment. Injecting additional aqueous lignosulfonate increases the efficiency of a sulphuric 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 [39, 40].

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 a 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.

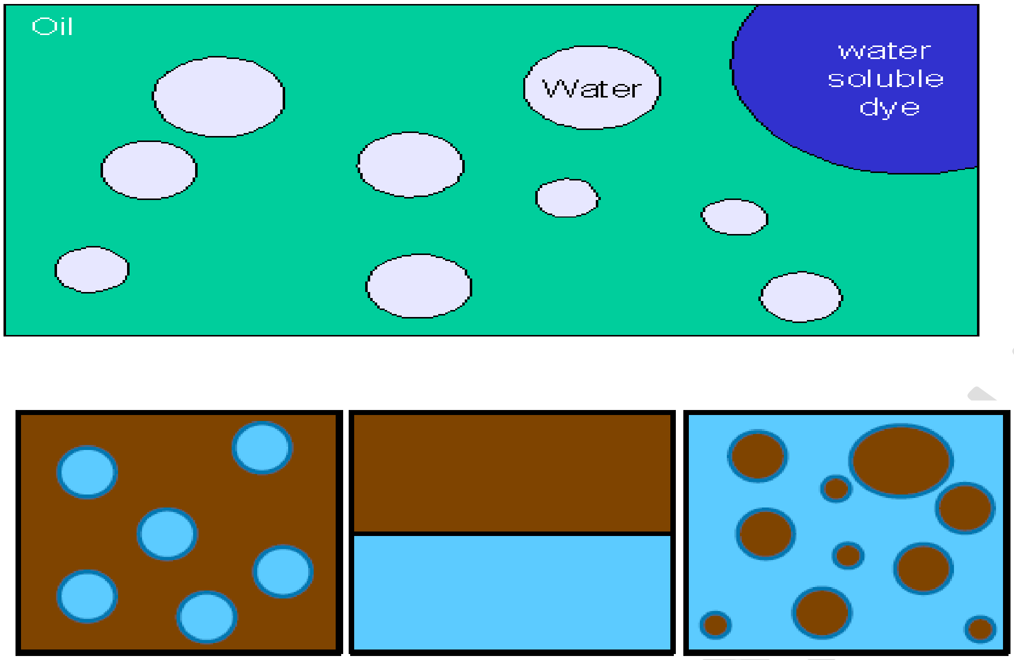


Plate 6. Representation of types of emulsions

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-watr interface. In addition, time must be allowed for the coalesced droplets to separate in phases. 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.

Breaking the emulsions, causes bulk of the water to 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.

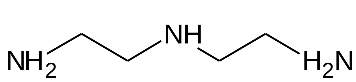
Prior to refining operation, crude oils are usually desalted by emulsification with fresh water, followed by demulsification. This is because crude oils with high salt contents might lead to breakdown and corrosion during refining, and an emulsion breaker, or demulsifier, is used to break the emulsion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

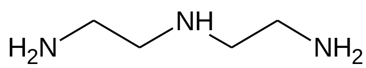
In crude oil production, demulsifiers are usually injected at the processing facilities before the separator. Emulsions that are slowly resolved need adequate time to separate. The fluids are hotter upstream, thus will result in faster emulsion resolution. Often, a range of demulsifiers and blends are 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 possess 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.

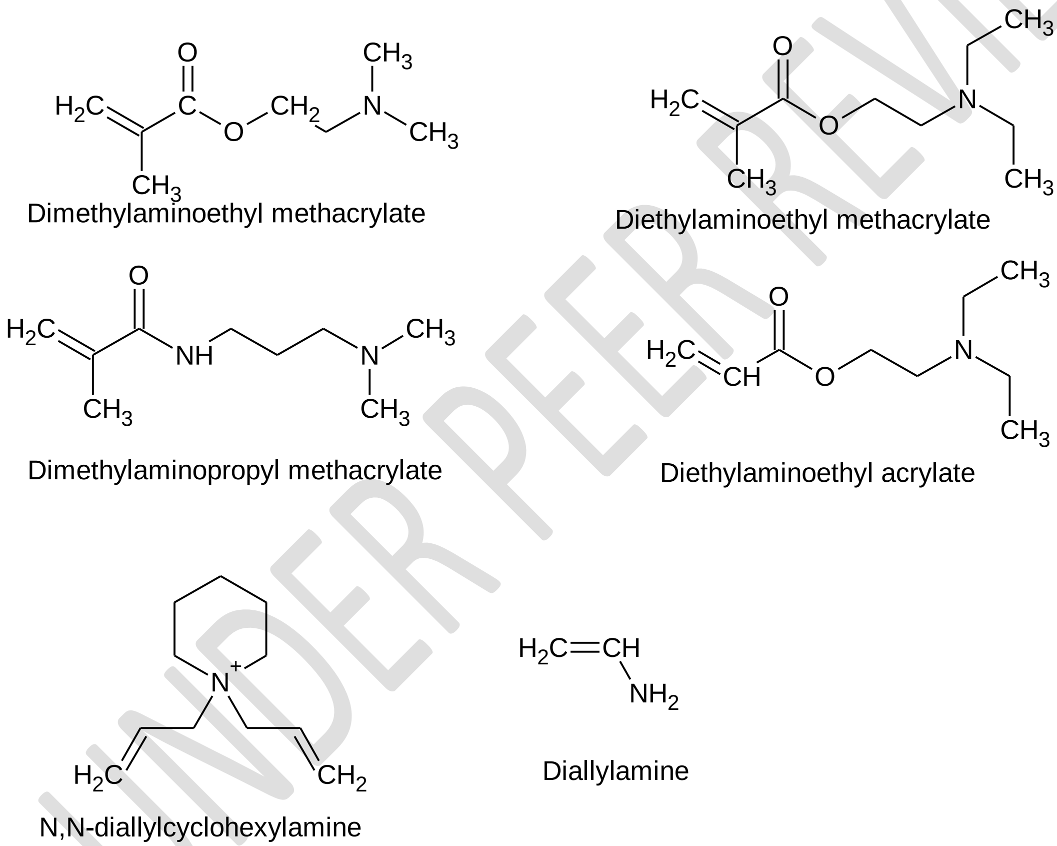




N-(2-aminoethyl)ethane-1,2-diamine

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 [41]. 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 sorbital hexaester of an aliphatic monocarboxylic acid, and propylene glycol ether as solvent [42]. 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 advert 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 [43].

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. This indispensable and vital information is 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 programs 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 operate at lower costs, obtaining maximum efficiency, process optimization and enhanced productivity in the oil and gas industry.

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