

## Technical Bulletin

# Products for Enhanced Oil Recovery

Huntsman is a global supplier of surfactants and other chemicals widely used in oilfield operations. Included are Enhanced Oil Recovery (EOR) products designed to meet the challenges of varying reservoir, injection water, and crude oil properties.

The key to a successful EOR formulation is to carefully select the components that provide ultra-low interfacial tension (IFT) under reservoir conditions. Achieving ultra-low IFT greatly reduces capillary forces that trap oil.

Huntsman's leadership position comes from its mix of technologies, world scale manufacturing capabilities, and global distribution network.

## Important Technologies

- **Alkylation:** Production of  $C_{14} - C_{30}$  alkylaryl compounds for use as hydrophobes that interact favorably with crude oil. When sulfonated, these long chain alkylaryl compounds are used as primary surfactants.
- **Alkoxylation:** Reaction of propylene oxide (PO) and ethylene oxide (EO) with active alcohols to produce nonionic surfactants and intermediates for further reaction.
- **Sulfation / Sulfonation:** Addition of a sulfate group to an alkoxyated molecule or a sulfonate group to an alkylaryl molecule.

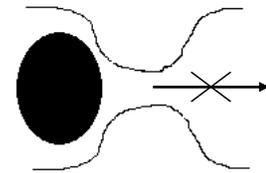
Using these technologies, Huntsman manufactures a variety of products for use as primary surfactants, co-surfactants and co-solvents.

## Primary Surfactants

These workhorse surfactant molecules must be chosen carefully to match the hydrophobe to the crude oil. The primary surfactant should also be able to withstand reservoir conditions and be compatible with the injection water.

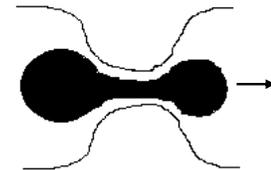
Huntsman offers three types of primary surfactants: alkylaryl sulfonates, extended chain surfactants and nonionic surfactants.

Alkylaryl sulfonates are well known for their durability and thermal stability. With the help of co-surfactants, they can tolerate moderate salinities. These materials are supplied in concentrates or custom-formulated solutions that require only dilution in the field.



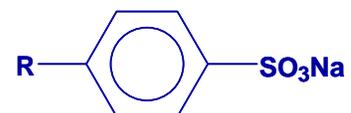
### High Interfacial Tension

Capillary Forces prevent oil from crossing through pore throats



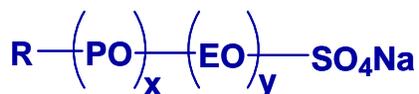
### Ultra-Low Interfacial Tension

Capillary Forces are reduced to near zero, allowing oil to move through pore throats



### Alkylaryl Sulfonates

Extended chain surfactants are very tolerant of salt and water hardness and are capable of producing ultra-low IFTs by themselves. The ether links "extend" the distance between the hydrophobe and the hydrophile.



### Extended Chain Surfactants

As ether sulfates, these surfactants are limited to use in reservoirs with moderate temperatures. Combining extended chain surfactants with alkylaryl sulfonates produces a very robust surfactant system that interacts well with crude oils and achieves ultra-low IFTs.

Nonionic surfactants are usually used as co-surfactants and co-solvents to enhance the properties of the primary surfactants. However, in reservoirs with very active oils, application of a nonionic surfactant may be all that is needed to mobilize the oil. Active crude oils will produce their own surfactants in the presence of alkali.

Primary Surfactants	Application
<b>Alkylaryl Sulfonates</b>	High temperature stability. Variety of crude oils. Low salinity conditions. (Higher salinity requires more co-solvent and maybe a co-surfactant.)
XOF-25S	Sulfonic acid of Alkylate H250 (C <sub>14</sub> – C <sub>30</sub> )
XOF-26S	Sulfonic acid of Alkylate A268 (85% C <sub>16</sub> -C <sub>18</sub> )
XOF-30S	Sulfonic acid of Alkylate 300 (C <sub>20</sub> -C <sub>24</sub> )
<b>Extended Chain Surfactants</b>	Temperature limit ~60°C. Light to medium crude oils. Optimal IFT at 2-3% salinity. Can be used as co-surfactants to reduce need for co-solvent.
XOF-202S	Linear alcohol propoxylate ethoxylate, sulfated, Sodium salt.
Other	Other compositions are under development.
<b>Nonionic Surfactants</b>	Temperature limited by cloud point. Light to medium crude oils. Very tolerant of salt and water hardness. Can be used as co-surfactants or co-solvents. Used when crude oil has plenty of surfactant character.
SURFONIC® L-series surfactants	Linear alcohol ethoxylates. SURFONIC® L24-5 and L24-12 surfactants have been used as primary surfactants in EOR.
SURFONIC® N-series surfactants	Nonylphenol ethoxylates with up to 40 EO
SURFONIC® DDP-series surfactants	Dodecylphenol ethoxylates with up to 14 EO

## Co-Surfactants

Co-surfactants are used to tailor the performance of the primary surfactant to the unique characteristics of the reservoir. They increase salt tolerance of the primary surfactant and allow ultra-low interfacial tensions to be achieved. The choice of co-surfactant will depend on the reservoir temperature, crude API gravity, crude composition, and the total dissolved solids (TDS) of the injection water.

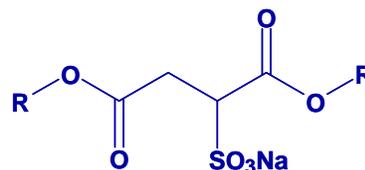
One particular product that works well in a majority of situations is XOF-200. This product is considered a "universal co-surfactant" and will help generate a very robust formulation.



**Alcohol Ethoxylates**



**Alkylaryl Ethoxylates**

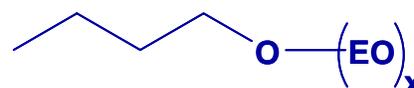


**Dialkyl Sulfosuccinates**

Co-Surfactants	Application
<b>Sulfosuccinates</b>	Excellent wettability. Salt and water hardness tolerance. Act to compatibilize packages. Temperature limited to ~ 80°C (break down into useful alcohols).
XOF-200	Sodium salt of dimethylamyl sulfosuccinate
SURFONIC® DOS-series surfactants	Sodium salt of dioctyl sulfosuccinate. More hydrophobic than XOF-200. Available in different solvent systems.
<b>Nonionic Surfactants</b>	Temperature limited by cloud point. Act to increase salt and water hardness tolerance.
SURFONIC® L-series surfactants	Linear alcohol ethoxylates.
SURFONIC® N-series surfactants	Nonylphenol ethoxylates with up to 40 EO
SURFONIC® DDP-series surfactants	Dodecylphenol ethoxylates with up to 14 EO

## Co-Solvents

One of the more recent discoveries in EOR is the need to have a homogeneous EOR package. Successful EOR depends on the presence of the surfactants at the interface between the injection water and the crude oil. A non-homogeneous EOR package indicates that some of the components (or their combinations) are insoluble. Insoluble materials may have a hard time flowing through the formation and might plug pore throats.



**Short Chain Alcohol Ethoxylates**

Co-Solvents	Application
<b>Short Carbon Chain Alcohol Ethoxylates</b>	Act to compatibilize packages containing surfactants that have large hydrophobes and reduce viscosity of microemulsions. SURFONIC® L4 series solvents have an oligomer distribution that mimics the distribution of crude oil composition.
SURFONIC® L4-1 solvent	<i>n</i> -butanol + 1 EO
SURFONIC® L4-2 solvent	<i>n</i> -butanol + 2 EO. Offers best balance of hydrophobe and hydrophile. Widely tested.
SURFONIC® L4-3 solvent	<i>n</i> -butanol + 3 EO. More hydrophilic than L4-1 and L4-2.
SURFONIC® L6-6 solvent	<i>n</i> -hexanol + 6 EO. Co-solvent with co-surfactant credit.
SURFONIC® EH-2 solvent	2-ethylhexanol + 2 EO. Large branched alcohol.

## Carbon Dioxide (CO<sub>2</sub>) EOR

Work is underway to develop surfactants for CO<sub>2</sub> EOR for use in a variety of situations:

- Water-soluble surfactants for producing foam
- CO<sub>2</sub>-soluble surfactants for producing foam
- CO<sub>2</sub>-soluble surfactants that mobilize oil. (WTO Pat. App. No. WO2009/094285 A1)

As more anthropogenic CO<sub>2</sub> is captured, these types of surfactants will allow CO<sub>2</sub> EOR to be used in more fields and with more difficult oils.

## Other Resources

- **Surfactant Screening for EOR:** Huntsman can test surfactants for injection water compatibility and perform IFT testing on a Dataphysics SVT 20N Spinning Drop Tensiometer.
- **Custom Surfactants:** As an independent company, Huntsman is free to enter into joint Development Partnerships to develop and produce unique molecules.
- **Other Oilfield Chemicals:** Huntsman offers an extensive line of production chemicals for oilfield use.
- **Local Sourcing:** Huntsman has a global distribution network and, in some cases, can provide regionally manufactured materials.

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