

## Vinylsulfonate-vinylamide copolymers and cross-linkable modifications thereof - Up-to-date chemicals for HTHP drilling, cementing and completion fluids -

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### ABSTRACT

In conventional drilling at temperatures up to 300 °F with water-based drilling fluids carbohydrate based polymers like starches and CMC/PAC are used for rheology stabilization and for fluid loss control. Under HTHP conditions (300 °F - 400 °F) these polymers fail because of their chemical structure which involves acetal linkages.

Fully synthetic co- and terpolymers with only carbon-carbon bonds in the backbone based on vinylsulfonate-vinylamide type monomers provide the necessary thermal stability for HTHP conditions. Even up to 450 °F, in particular cases even 500 °F could be managed with these polymers. Unlike for instance CMC they also tolerate bivalent cations up to saturation. Thus nowadays deep and hot wells can be drilled safely with water based muds with vertical depths of 16,000 feet and more. The same class of HTHP polymers is also used for cementing of deep and ultra deep wells.

Recently cross-linkable versions of vinylsulfonate-vinylamide type polymers have been developed. Cross-linking is achieved at temperatures up to 400 °F with metal salts or chelates, e.g. based on aluminum, titanium or zirconium and yields high temperature stable gels. More viscous solutions up to non-flowing, but deformable ("ringing") gels can be obtained by varying both polymer and cross-linker. Cross-linking can be delayed or shifted to higher temperatures with suitable retarders.

### INTRODUCTION

The demand for oil and gas will increase and the production from mature reservoirs will decline. The overall production needs to grow. Therefore production methods must be improved, more wells need to be drilled and more new reservoirs need to be developed. This will also include more drilling for deeper and hotter wells. Thus the demand for systems and products with higher thermo stability will increase.

### DRILLING MUDS

Drilling muds are essential for successful drilling. They need to be carefully designed and maintained because they have to fulfill many complex requirements, for instance:

- Adequate rheology for the removal of rock cuttings via the annulus and for the separation in the subsurface devices.
- Reduce the fluid loss into the formation by forming a thin filter cake with low permeability.
- Cool and lubricate the drill bit and drill string and reduce friction between drill string and formation.
- Stabilize the non-cased borehole by avoiding shale swelling.
- Minimize formation damage in the productive formation (pay zone).
- Ensure adequate evaluation of the formation (MWD well logging).
- Minimize the impact on the environment.

The suspension of cuttings under static conditions, their removal from the borehole, their transport to the surface installations and their separation requires a thixotropic - shear thinning or pseudo plastic - fluid rheology. In water based muds these basic rheological properties are achieved by special clays like bentonite, predominantly a sodium montmorillonite. The clays also reduce the fluid loss by forming a thin filter cake with low permeability to the wall of the borehole, thus preventing the invasion of the fluid into the formation. To control the rheological properties of aqueous clay suspensions, also in the presence of electrolytes, special polymers, mostly anionic polyelectrolytes, are necessary.

Clays like montmorillonite are layered aluminosilicates which are negatively charged within the layers. The negative charges are compensated by - exchangeable - cations between the layers. These clays consist of plate like particles with negative partial charges on the surfaces (faces) and positive partial charges on the edges.

When sodium bentonite is dispersed in water it swells significantly and finally a complex equilibrium between aggregated, dispersed and flocculated particles is formed.

The partial flocculation of the hydrated clay results in a "house of cards" structure. This structure impairs the basic thixotropic rheological properties of drilling muds because of its shear behavior:

- Partial gelation resp. flocculation under static conditions, high viscosity at low shear rates to avoid sedimentation of the cuttings.
- Shear thinning at higher shear rates to facilitate pumpability and circulation of the mud, providing an adequate plastic viscosity for the transport of the cuttings.

## Mud Additives

### Thinners / deflocculants

In case the gelation and the viscosity profile of the mud is too high, the flocculated particles need to be deflocculated. Deflocculation is achieved by anionic polyelectrolytes with short chain lengths and molecular weights below 100,000 Daltons.

**Table 1:** Operability limits of mud additives  
- Thinners / Deflocculants

Polyphosphates	175 °F
Quebracho / Tannins	250 °F
Lignosulfonates	340 °F
Lignites	400 °F
Styrene sulfonic acid based copolymers	400 °F
Polyacrylates (modified)	400 °F
Ketone / aldehyde / sodium bisulfite polymer	400 °F

These dispersing agents, also called thinners partly neutralize the electrochemical charges on the clays. Thus they deflocculate the house of card structures. Polyphosphates, polyacrylates, tannins, lignites and lignosulfonates are the most commonly used thinners/dispersants.

Deflocculation also aids to reduce the fluid loss by allowing the clay particles to lay flat in the filter cake.

### Protective colloids

To avoid an unstable rheology by the influx of electrolytes from the formation, protective colloids are added to drilling muds. These are water soluble polymers with molecular weights in the range of 100,000 - 1,000,000 Daltons which stabilize the "house of cards" state of the clays.

**Table 2:** Operability limits of mud additives  
- Protective colloids / viscosifiers

Starch and Derivatives	250 °F
Carboxymethylcellulose / PAC	300 °F
Xanthan Gum	300 °F
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Polyacrylamides / PHPA	400 °F
VS / VA copolymers	>400 °F
Other AMPS based copolymers	>400 °F

Protective colloids are also mainly anionic polyelectrolytes. The anionic groups interact with the positive charges of the edges of the clay platelets. Depending on the molecular weight and the adsorption behavior, these polymers

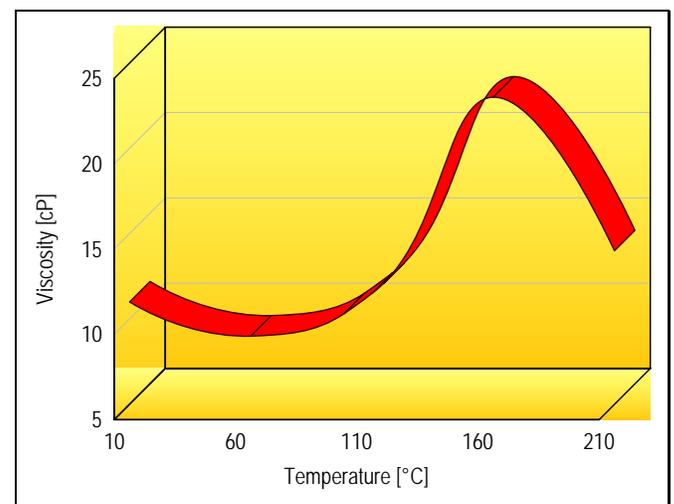
either disperse flocculated clays or stabilize the flocculated state of the clay suspension in the presence of electrolytes. Protective colloids are commonly called fluid loss additives because they promote the formation of a stable, thin and impermeable filter cake on the wall of the wellbore.

Carboxymethylcellulose - CMC - and PAC (Poly Anionic Cellulose), a CMC with a higher degree of substitution are the most commonly used protective colloids and fluid loss additives in water based drilling muds.

Like starches, CMC/PAC and also xanthan gum are carbohydrate based polymers. Their backbone of is based on anhydro glucose units which are linked  $\beta$ -glucosidic. The weak points of this backbone are the repeating acetal (-O-C-O-) linkages which are susceptible to both oxidative and thermal cleavage at temperatures above 280 °F. Whereas the oxidative degradation can be suppressed by radical scavengers, the thermal degradation limits the application of carbohydrate based polymers in general.

Another limitation is the carboxymethyl substitution which is sensitive to high concentrations of bivalent calcium and magnesium cations in general.

In wells with vertical depth >13,000 feet, in "hot spots" even already >10,000 feet, temperatures of 300 °F up to 500 °F are occurring. Under these conditions, carbohydrate based polymers like CMC/PAC fail because of oxidative and thermal degradation. The drilling muds will lose the necessary rheological properties and also the fluid loss will increase to unacceptably high levels.



**Figure 1:** Thermo-gelation of bentonite

Also the thermo-gelation of bentonite, occurring at temperatures around 300 °F is not suppressed by CMC. The mud gels and it becomes difficult or even impossible to restart the drill string after drill string reconnections or drill bit exchanges. This could mean the loss of the well respectively the loss of a couple of million dollars.

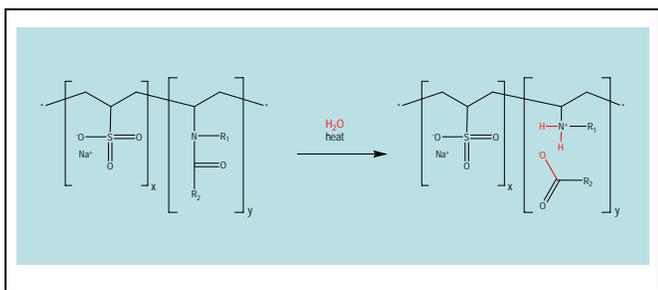
### Fully synthetic polymers

The stability at temperatures from 300 °F to up to 450 °F and even 500 °F can only be achieved with polymers with a backbone consisting of carbon-carbon bonds only. The most common polymers of this type are partially hydrolyzed polyacrylamides (PHPA). Their carboxylate functions are required for the interaction with clays but make them sensitive to calcium ions. At elevated temperatures, the calcium sensitivity of PHPA even increases because of the increasingly rapid hydrolysis of the acrylamide moiety creating even more carboxyl groups.

So PHPA is only suitable for calcium-free drilling mud systems which are not common in practice.

### Vinylsulfonate-vinylamide copolymers

Vinylsulfonate-vinylamide copolymers were expected to be thermostable and to be highly tolerant to calcium and magnesium because of their different hydrolytical behavior:



**Figure 2:** VS-VA hydrolysis

The vinylsulfonate group is stable to hydrolysis, whereas the vinylamide group hydrolyses to an amine group which helps in the interaction of the resulting polymer with the clay lattices in the mud. The calcium sensitive carboxyl group is split off and forms a soluble carboxylate with the alkali present in the mud.

The first experimental product was a copolymer of sodium vinyl sulfonate and a vinylamide which already showed the desired properties. Because of the poor copolymerization behavior of sodium vinylsulfonate, the necessary molecular weights were difficult to achieve and the product was not an economic success. But VS-VA copolymers became the synonym of this type of polymers.

The break through was achieved when ATBS (Acrylamido Tertiary Butyl Sulfonic Acid) became available on commercial scale.

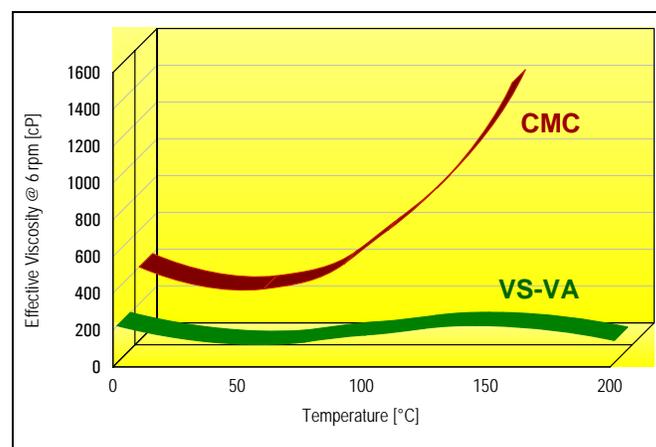
With the acrylamide substructure in the ATBS molecule it is possible to achieve medium to high molecular weights up to the 107 Dalton range if desired. The amide subgroup is sterically shielded by the bulky branched butylsulfonate group. This results in a much higher hydrolytic stability than

that of acrylamide itself.

Our vinylsulfonate-vinylamide type copolymers are marketed under the brand name <sup>®</sup>Hostadrill. They are terpolymers based on ATBS and vinylamide in the molecular weight range of 500,000 - 1,000,000 Dalton. They have the desired properties needed for high temperature/high pressure (HTHP) drilling with water based muds.

- Temperature stability up to 450 °F, under certain circumstances even up to 500 °F.
- Tolerance to calcium and magnesium cations up to saturation.

This enables optimum rheology and fluid loss control under these hostile conditions.



**Figure 3:** Rheology stabilization by VS-VA copolymers

The thermo-gelation of bentonite is effectively suppressed by deflocculation at high temperatures.

This efficiency has been proven in many years of field practice. No gelation of the mud occurs even after a circulation stoppage when the mud has to withstand up to 50 hours and more at bottom hole temperatures up to 400 °F and more.

Apart from the monomer composition a special precipitation polymerization process is the key for the performance of the polymer. Various attempts to obtain the same application properties by less complicated and also less costly processes have not been successful.

### Environmental aspects

Vinylsulfonate-vinylamide copolymers are non-toxic, the LD50 to rats is above 5,000 mg/kg. Above all their favorable aquatic toxicity profile makes them suitable for offshore drilling with water based muds in environmental sensitive regions. They help to avoid the use of oil based muds with their detrimental effect of oil-wetted cuttings when disposed in the sea.

With vinylsulfonate-vinylamide type copolymers, the use of chromium containing lignosulfonates can be avoided.

Because of their polymer structure, VS-VA copolymers are not readily biodegradable. According to recent findings, the biodegradability can be improved by slight modification of the polymer composition.

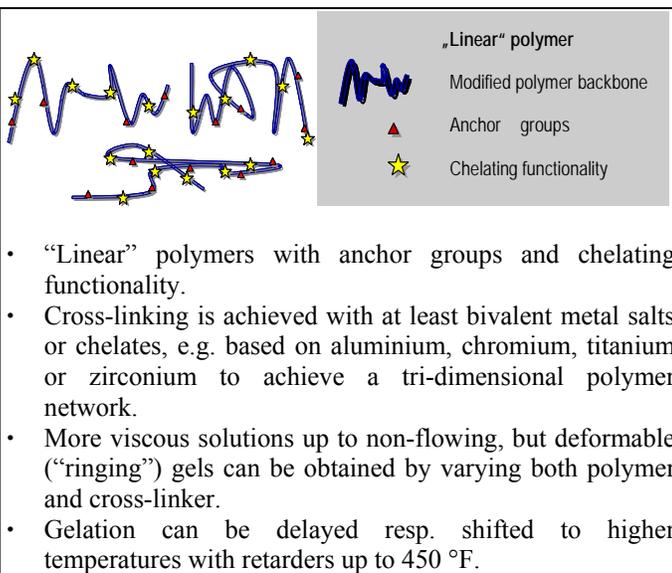
## CEMENTING

Vinylsulfonate-vinylamide type polymers with similar monomer composition are also widely used as fluid loss additives for cementing of oil and gas wells.

®Hostamer grades provide efficient fluid loss control to cement slurries over a very broad temperature range of 50 up to 500 °F. Fluid loss additives for cementing must tolerate high electrolyte concentrations and pH values above 12. They must be compatible with other additives like dispersants and retarders, should not affect the setting behavior and the compressive strength of the cement and must prevent from micro-channeling.

## CROSS-LINKABLE VS-VA COPOLYMERS

By the addition of small amounts of a suitable comonomer, chelating functionality can be incorporated. Thus cross-linkability can be achieved with at least bivalent metal salts like acetates or with metal chelates like for instance lactates based on aluminum, chromium, titanium or zirconium.



**Figure 4:** Cross-linkable VS-VA copolymers – Principle

By variations of the polymer’s cross-linkability and the type or amount of cross-linker more viscous solutions up to non-flowing, but deformable (“ringing”) gels can be created.

Our cross-linkable polymers are anionic/nonionic polyelectrolytes with medium to high molecular weight. They are soluble and stable in brines and in acids, thus also suitable

for acidizing. Their high thermo stability up to 450 °F allows gelation at high temperatures as well as the formation of high temperature stable gels.

By the addition of suitable retarders the gelation can be delayed respectively shifted to higher temperatures.

Cross-linkable VS-VA polymers offer a broad variety of applications at high temperatures such as:

- proppants suspension and transport in fracturing fluids,
- retardation by gelation of acids in acidizing,
- control of fluid loss by gelation of heavy brines in completion and workover fluids, prevention of lost circulation in drilling and
- relative permeability modification for water control and selective or total water shut off.

## CONCLUSION

Vinylsulfonate-vinylamide based polymers for drilling and cementing have become industry standards. Because of their relatively high price they are sometimes called “gold dust”. In the case of drilling, they are only used when the demands on the drilling mud can no longer be met by conventional mud additives or oil based muds are prohibited because of environmental regulations. Cross-linkable VS-VA polymers are providing a new interesting potential for HTHP applications. Because of the HTHP potential for the future exploration and production of oil and gas we see a good perspective for the “gold dust for the black gold”.

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