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Inhibition of Hydrolytic Degradation in Ester-Based Invert Emulsion Drilling Fluids

Jay P. Deville, Halliburton

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Abstract

Hydrolysis is a detrimental pathway resulting in the decomposition of esters in ester-based invert emulsion drilling fluids. The products of hydrolytic degradation of esters, namely alcohols and carboxylate salts, can adversely affect fluid performance and properties. Additionally, hydrolysis reaction products, particularly low molecular weight alcohols, can generate HSE issues in terms of both increased toxicity of the fluid and an increased hazard to rig personnel monitoring the fluid.

Although ester hydrolysis can take place any time esters are in contact with water, the reaction is accelerated under both alkaline and acidic conditions. Hydrolysis is also exacerbated at elevated temperatures. As a result ester-based drilling fluids are generally utilized with minimal lime concentrations and in wellbores with temperatures of 300ºF or less.

Chemical additives that can be incorporated into an ester-based drilling fluid and inhibit ester hydrolysis have been developed. Greater than 90% reductions in the amount of ester hydrolysis were observed in the presence of these additives. Hydrolytic protection of the valuable esters is conferred because the additives are more easily hydrolyzed than esters, thus offering a more kinetically favorable pathway for hydrolytic species. The inhibition of ester hydrolysis in ester-based invert emulsion fluids potentially allows for the application of these advantageous fluids in more thermally demanding environments. Data on the inhibition of hydrolysis in ester-based invert emulsion fluids with chemical additives along with a discussion of the applicability of these additives to protect other drilling fluid additives is reported herein.

Introduction

Ester-based base oils have amassed an excellent track record as an environmentally responsible component of invert emulsion drilling fluids.[1] Pure ester base oils as well as ester blends have been used with particularly great success in clay-free, high performance invert emulsion fluids (IEF).[2] Esters used are generally derived from a fatty acid and a low molecular weight alcohol.

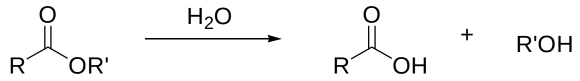
Despite the advantages of ester-based IEFs, application is generally limited to wellbores with a bottomhole temperature of 300ºF or less. This limitation is imposed as a result of thermal degradation, more specifically hydrolytic degradation that is more prevalent at higher temperatures, of the ester molecules.[3] The hydrolysis of esters in ester-based IEFs can adversely affect fluid properties, negatively impact the toxicity of the fluid, and generate HSE hazards for rig personnel.

Reducing the amount of ester hydrolysis that occurs in a fluid system can allow for application of these environmentally-advantageous fluids in more thermally demanding environments.[4] Development efforts toward a chemical additive capable of inhibiting hydrolytic degradation of esters are described in this paper. In describing these endeavors the following topics will be discussed:

- General discussion of hydrolysis
- Adverse affects of ester hydrolysis in ester-based IEFs
- Chemical treatments for inhibiting hydrolysis

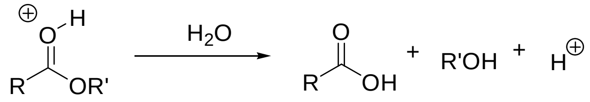
Hydrolysis

Hydrolysis is a reaction pathway that can operate on a variety of substrates pertinent to drilling fluids including esters, amides, and acetals. Fundamentally, hydrolysis is the reaction of a molecule with water. The hydrolysis of a generic ester is shown below (R and R' = generic alkyl groups).

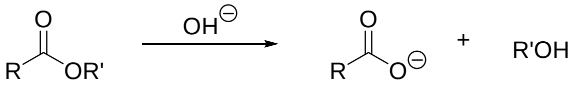


The hydrolysis reaction degrades an ester into a carboxylic acid and an alcohol. While the uncatalyzed reaction shown can occur, particularly at elevated temperatures when greater thermal energy is available, hydrolysis is accelerated by both acidic and basic conditions.

Under aqueous acidic conditions, a more reactive protonated ester is formed. This makes the subsequent attack by water a more facile process. The hydrolysis of an ester under acidic conditions is a reversible process and the alcohol and carboxylic acid can react to reform the ester. These conditions are not commonly seen in drilling fluids.



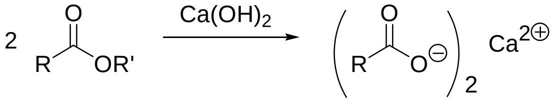
Alkaline conditions for ester hydrolysis involve the attack of the more reactive hydroxide ion, instead of water, on the ester substrate:



It is important to note that under alkaline conditions, the carboxylic acid formed will exist in its deprotonated form, a carboxylate. As a result, hydrolysis under basic conditions is an irreversible process and the deprotonated carboxylic acid and the alcohol can not reform the ester.

Effects of Ester Hydrolysis in IEFs

As can be seen in the reactions outlined in the preceding section, hydrolysis of an ester produces a carboxylic acid and an alcohol. Each of these products poses problems in IEFs used as drilling fluids. In the presence of lime, hydroxide ion is available for a base-promoted ester hydrolysis. As shown previously, base-promoted ester hydrolysis irreversibly produces a deprotonated carboxylic acid. In the presence of the divalent calcium from the lime produces calcium soaps (and alcohol which is omitted for clarity).



These calcium soaps generally have a negative impact on IEF rheological properties.[3] Fluids in which hydrolysis has occurred to produce these calcium soaps exhibit significantly higher rheology to an extent that can render the drilling fluid intractable.

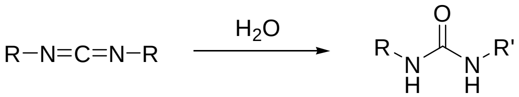
When this problem was observed in the use of ester-based IEFs, it became good drilling practice to simply limit the excess lime in the system. Limiting lime has two advantages in that it reduces the concentration of hydroxide available for base-promoted hydrolysis of the esters while at the same time removing calcium that reacts with hydrolyzed esters to produce the deleterious calcium soaps.

While limiting excess lime concentrations certainly eases the threat of ester hydrolysis, significant hydrolysis can still occur via the uncatalyzed, direct reaction of ester and water as wellbore temperatures increase. This mode of reactivity produces carboxylic acids, which in the absence of lime may not be as detrimental to the fluid. Also produced in this reactivity mode are alcohol molecules. These alcohol molecules are generally low molecular weight which creates a number of problems in an IEF. The low-molecular weight alcohols are often toxic, which is particularly problematic for a fluid chosen in large part for its favorable environmental properties.[1] Furthermore, these low-molecular weight alcohols are often volatile, leading to pungent odors and potentially flammable vapors at the surface. This creates a HSE hazard for rig personnel.

Chemical Inhibitors of Hydrolysis

Given the utility of ester-based IEFs and the limitations imposed by hydrolytic degradation of the esters, a chemical additive capable of inhibiting ester hydrolysis was sought. Such an additive would potentially allow for ester-based fluids to be applied in more thermally-demanding wellbores and hence extend the useful working temperature range of ester-based IEFs. Additives capable of kinetically inhibiting hydrolysis were targeted. These materials would protect ester components by simply being more easily hydrolyzed. The presence of the more easily-hydrolysable additive would in essence be sacrificed to stave off hydrolysis of the esters. It is important that any additive chosen does not hydrolyze to form products that will be detrimental to the mud properties or generate HSE issues.

Based on these criteria, carbodiimide chemistry was explored. Carbodiimides are readily hydrolyzed to form urea compounds.



When these materials react with water, only a single product is formed, which depending on the R groups can be non-volatile. Polymeric carbodiimides were evaluated for this study to ensure that the hydrolysis products were not volatile and hence not capable of posing the same potential HSE problems the low molecular weight alcohols from esters present.

Testing Protocol

Two polymeric carbodiimide additives were tested as hydrolysis inhibitors. Inhibitor A is a solid material of higher molecular weight and Inhibitor B is a viscous oil of lower molecular weight. Each was tested at 5 lb/bbl loadings. The additives were tested for efficacy at inhibiting hydrolysis by measuring the alcohol concentration in the fluid before and after static aging at 370ºF. This temperature was chosen to be high enough to ensure significant hydrolysis would occur in an uninhibited system. Samples were aged for 16 hours. Alcohol content was measured by a well-established GC/MS method.

Testing Results

Base Oil Testing

The carbodiimide inhibitors were initially tested in an ester-containing base oil without added water. Due to the absence of water, little hydrolysis was expected in the carbodiimide-containing samples or the control which was simply ester-containing base oil.

The samples were aged according to the test protocol. Little alcohol was produced in each sample, indicative of little hydrolysis (**Figure 1, Table 1**). The ester-containing base oil was found to have 35 ppm alcohol prior to heating.

Testing in Simple IEF Systems

Testing continued with carbodiimide inhibitors in a simple invert-emulsion system comprised of ester-containing base oil, a non-hydrolyzable emulsifier (8 lb/bbl), and a 250,000 ppm $CaCl_2$ brine. The oil/water ratio was 90:10. Due to the presence of water, this represents a true test for the hydrolysis inhibitors. As expected, in the presence of water a greater amount of hydrolysis occurred for all samples after aging (**Figure 2, Table 2**). However, the systems containing the inhibitors showed a marked reduction (both greater than 90%) in the amount of ester hydrolysis that occurred, as measured by alcohol content. Clearly, in these simplified fluid systems the carbodiimide additives are effective at reducing the amount of ester hydrolysis that occurs.

Testing in Simple Lime-Containing Systems

A more demanding set of conditions was probed as 3 lb/bbl of lime was added to the simplified system described in the preceding paragraph. Recall that lime is particularly damaging to esters in that the hydroxide facilitates hydrolysis and the calcium forms calcium soaps with the hydrolyzed product. As expected, the alcohol content was substantially higher in the lime-containing fluids indicating a greater degree of hydrolysis. Despite these forcing conditions, the inhibitors were still able to successfully reduce hydrolysis by greater than 40% (**Figure 3, Table 3**) over the control. In fact, Inhibitor A showed less hydrolysis in this test with lime than the inhibitor-free sample showed with only water (cf. **Figure 2** and **Figure 3**).

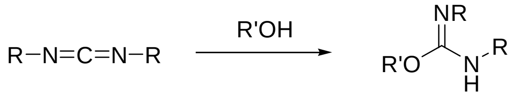
Whole Mud Testing

After observing favorable results with the carbodiimide inhibitors in simplified systems, data was collected in a whole mud. The efficacy of the inhibitors was evaluated in a 17 lb/gal clay-free, high performance IEF with an ester-containing base oil (**Table 4**). Interestingly, although both Inhibitors A and B performed similarly in simplified testing, only Inhibitor A proved effective in a whole mud (**Figure 4, Table 4**) producing a nearly 90% reduction in the amount of alcohol produced after aging at 370ºF. The reasoning for the difference in the activity of the inhibitors in the whole-mud test is not entirely clear but may be due to the way the materials interact with the solids that are present in the whole mud, but absent from the simplified systems.

Of further interest are the fluid properties in the presence of the hydrolysis inhibitors. The sample containing Inhibitor A displayed comparable rheological properties to the control sample containing no inhibitor (**Table 4**). Interestingly, the Inhibitor A sample showed less change in high shear rheology and plastic viscosity than the control, possibly as a result of reduced hydrolytic activity. The sample containing Inhibitor B showed a more pronounced thinning effect, possibly as a result of its wetting or other interactions with solids.

Inhibition Confirmation

The data presented thus far clearly indicates that the amount of alcohol present in ester-containing systems after aging at elevated temperature is significantly less in systems containing an inhibitor. The assumption made is that since alcohol is produced from hydrolysis of the esters, then the alcohol concentration is a measure of hydrolysis. The lower alcohol concentrations in the presence of the inhibitors were indicative of reduced ester hydrolysis. Another possibility was considered, namely that the inhibitors were not reducing the amount of hydrolysis but instead were reacting out the alcohol after hydrolysis occurred.



If this occurred the reduced alcohol concentrations seen in the presence of the inhibitors would not be a reflection of reduced hydrolytic activity, but instead an effective binding of the alcohol after it was produced. To test this, samples of ester-containing base oil were spiked with alcohol prior to aging. The samples were then aged according to the standard procedure, with the expectation that if the alcohol was reacting with the inhibitors then the inhibitor containing samples should show a significant reduction in the alcohol content. As the data indicates, any direct reaction of the inhibitors with the alcohol is minimal at best (**Table 5**). This further supports the notion that the carbodiimides are acting truly as hydrolysis inhibitors.

Conclusions

Chemical additives capable of inhibiting hydrolysis of esters in ester-based IEFs have been shown to be effective, reducing the amount of hydrolysis by more than 90% in whole muds. These polymeric carbodiimide additives, which produce benign urea compounds and no volatile organics, offer inhibition by being more readily hydrolyzed than esters. Use of these materials potentially allows for application of environmentally-advantageous ester-based IEFs in more thermally-demanding wellbores. While the focus of study in this paper was inhibition of hydrolysis of esters in base oils, the protective effects of these agents could potentially be applied to other hydrolysable fluid components such as emulsifiers, wetting agents, and fluid loss control polymers.

Acknowledgments

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Tables

Table 1. Alcohol Content of Ester-Containing Base Oil Samples after Aging at 370º F for 16 hours

Sample	**A**	**B**	**Control**
Ester-Containing Base Oil, bbl*	1	1	1
Inhibitor A, lb	5	–	–
Inhibitor B, lb	–	5	–
Static Aged at 370 ºF, hr	16	16	16
% by wt alcohol	**0.0059**	**0.0080**	**0.0053**
ppm alcohol	**59**	**50**	**53**

*-Base oil contained 35 ppm alcohol prior to aging

Table 2. Alcohol Content of Ester-Containing Simplified IEF Samples after Aging at 370º F for 16 hours

Sample	**A**	**B**	**Control**
Ester-Containing Base Oil, bbl	0.9	0.9	0.9
250,000 ppm $CaCl_2$ brine, bbl	0.1	0.1	0.1
Emulsifier, lb	8	8	8
Inhibitor A, lb	5	–	–
Inhibitor B, lb	–	5	–
Static Aged at 370 ºF, hr	16	16	16
% by wt alcohol	**0.053**	**0.041**	**0.61**
ppm alcohol	**529**	**409**	**6133**

Table 3. Alcohol Content of Ester-Containing Simplified IEF Samples with Added Lime after Aging at 370º F for 16 hours

Sample	**A**	**B**	**Control**
Ester-Containing Base Oil, bbl	0.9	0.9	0.9
250,000 ppm $CaCl_2$ brine, bbl	0.1	0.1	0.1
Emulsifier, lb	8	8	8
Lime, lb	3	3	3
Inhibitor A, lb	5	–	–
Inhibitor B, lb	–	5	–
Static Aged at 370 ºF, hr	16	16	16
% by wt alcohol	**0.56**	**0.64**	**0.98**
ppm alcohol	**5556**	**6434**	**9804**

Table 4. Whole Mud Formulation and Properties Including Alcohol Content

Sample	**A**		**B**		**Control**	
Mud Weight, lb/gal	17					
OWR	90:10					
Ester-Containing Base Oil, bbl	0.52		0.52		0.52	
250,000 ppm $CaCl_2$ brine, bbl	0.068		0.068		0.068	
Emulsifier, lb	10		10		10	
Secondary Emulsifier, lb	1		1		1	
Filtration Control Polymer, lb	3		3		3	
Simulated Drill Solids, lb	20		20		20	
Weighting Agent, lb	497		497		497	
Inhibitor A, lb	5		–		–	
Inhibitor B, lb	–		5		–	
Hot Rolled at 150 ºF, hr	16	16	16	16	16	16
Static Aged at 370 ºF, hr	–	16	–	16	–	16
% by wt alcohol	**0.03**	**0.09**	**0.04**	**0.71**	**0.06**	**0.78**
ppm alcohol	**277**	**874**	**416**	**7129**	**626**	**7761**
Fann 35 Data at 120 ºF						
Plastic Viscosity, cP	48	44	37	37	43	52
Yield Point, lb/100 ft^2	8	16	0	6	19	13
10s/10m Gel Strengths, lb/100 ft^2	7/10	7/8	4/5	3/4	8/10	7/10
600 rpm	104	104	72	80	105	117
300 rpm	56	60	35	43	62	65
200 rpm	41	43	25	29	46	47
100 rpm	25	26	15	16	29	28
6 rpm	6	6	3	3	8	6
3 rpm	5	5	3	2	7	5

Table 5. Alcohol Spiking Experiments for Mechanism Check

Sample	**A**	**B**	**Control**
Ester-Containing Base Oil, bbl*	1	1	1
Inhibitor A, lb	5	–	–
Inhibitor B, lb	–	5	–
Static Aged at 370 ºF, hr	16	16	16
% by wt alcohol	**2.46**	**2.35**	**2.48**
ppm alcohol	**24,553**	**23,540**	**24,831**

*-Each sample was spiked with the same volume of alcohol

Figures

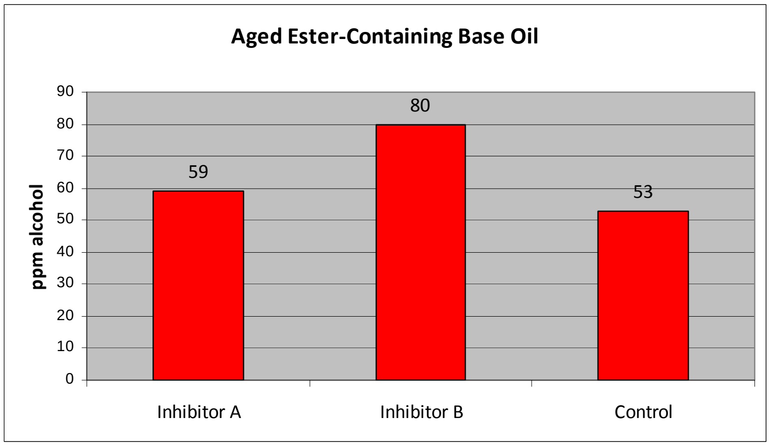


Figure 1. Alcohol Content of Ester-Containing Base Oil Samples after Aging at 370º F for 16 hours

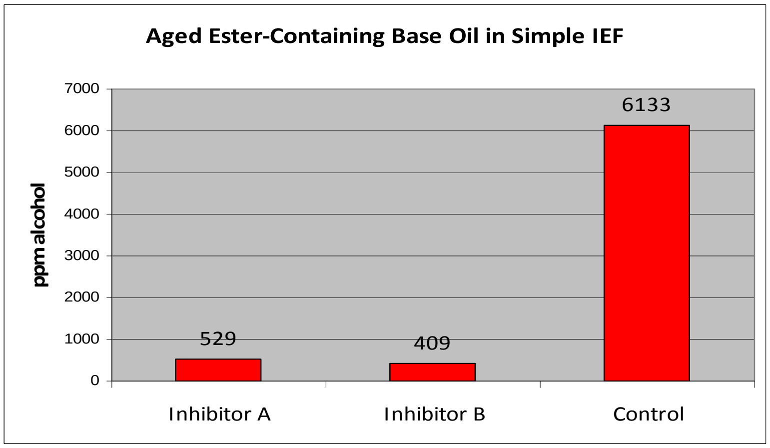


Figure 2. Alcohol Content in Ester-Containing Simplified IEF Samples after Aging at 370º F for 16 hours

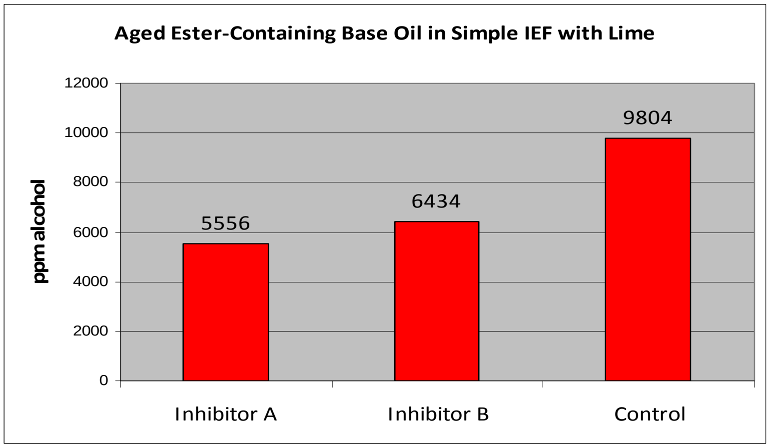
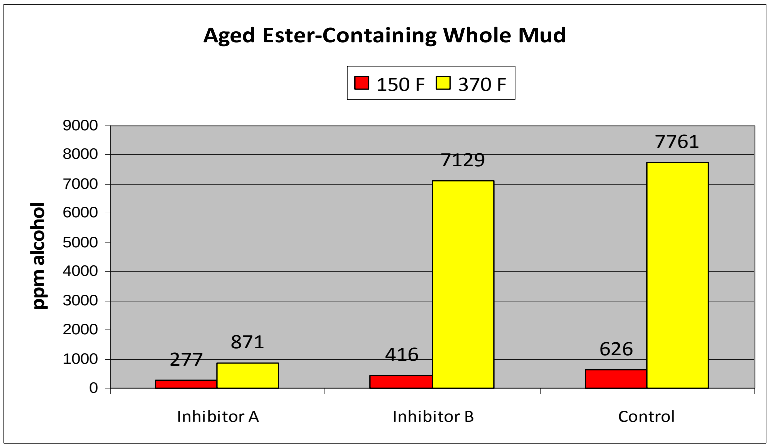


Figure 3. Alcohol Content of Ester-Containing Simplified IEF Samples with Added Lime After Aging at 370º F for 16 hours



. Figure 4. Alcohol Content in Ester-Containing Whole Muds After Aging at 150 and 370 ºF for 16 hours