NEW RESIN COATED PROPPANTS

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INTRODUCTION

The oilfield use of resin coating on proppants such as sand, glass beads and ceramics began in the middle 1970's. Applications include downhole use in both onshore and offshore oil and gas wells.

The initial idea was to pump a partially cured or curable resin coated proppant (RCP) in frac fluid into a well and let the elevated bottom hole temperature polymerize and bond the phenolic resin particles together. These bonded particles form a downhole filter or sheet of permeable sandstone in the fracture.

The earliest use was for sand control where resin coated particles were injected as a gravel pack. In 1976 the resin coated particles were first used as a small tail-in proppant in a hydraulic fracture treatment. Starting with small volumes this use gradually expanded to larger volumes until today large volumes of the frac proppant in many wells are resin coated. Resin coated materials replace both sand and ceramic proppants and have now grown to a frac market of many million pounds per year.

APPLICATIONS

Proppants are strong but brittle particles that at some closure pressure shatter or break. By resin coating any proppant with a phenolic formaldehyde resin chemically attached to the particle, the former brittle material becomes crush resistant.

This transformation is accomplished by taking away the point-to-point load on each particle and replacing it with a small pad of resin. Figure 1 illustrates this concept. Additional benefits of bonding are prevention of proppant flowback and minimization of embedment. The first resin coated proppants of the late 1970's had a single partially cured coat of resin. The first manufacturing of resin coated materials were carried out with a solvent coating process. This quickly changed to a hot coating process as volumes increased. The trade name of the first resin coated product used in hydraulic fracturing was Super Sand.

In 1981 the first precured resin coated sands appeared. Although they provided no bonding of the particles, they were stronger than sand. Their use grew to large volumes in several specific areas of applications.

In 1984 dual resin coated proppants were patented and introduced. These had a precured inner coat for crush resistance and an outer coat that was partially cured to bond together just in the fracture. The advantages are that crushing, embedment and flowback are prevented with these double resin coated particles. Also the multiple coatings were applied to ceramic materials as well as sands.

During 1990, the next evolutionary step in resin coated proppants was undertaken. A family of resin coated proppants was introduced to work at different depths in the well. This proppant system uses field proven technology and provides long term permeability in three closure stress ranges which are generally associated with shallow, intermediate, and deep oil or gas wells. Table 1 shows the products designed for each closure stress and depth.

When designing hydraulic fracture treatments, an important design factor is the long term permeability of the proppant in the fracture. Today oil or gas companies are buying long term permeability when they buy any proppant. With the 1990's PROPPANTS long term permeability of the curable resin coated proppants measure about 100 Darcy's in the closure stress range of each one. This is measured by standard independent lab tests all at the same conditions. These results are shown in Table 2.

Examples of long term permeabilities for 3 curable resin coated proppants versus closure stress at 250°F (20/40 mesh) are shown in Figure 2. These tests were carried out using standard long term tests with Ohio Sandstone walls and 2% KCl fluids. The proppants tested are standard production samples and have not been presieved. The typical sieve analysis for each of the 1990 products are given in Table 3.

Shallow to Intermediate Depths

For the shallow to intermediate depth wells, sand has always been used as a proppant. However, sand embeds and flows back very easily. Above 2000 psi closure stress and with elevated temperature some sand crushing is seen. Curable resin coating proppants (RCP) prevent this crushing, as well as flowback and embedment. In this depth and stress range a RCP such as SUPER LC^{TM} (low cost) proppant can replace sand.

It offers better conductivity and long term permeability than sand but eliminates migrating fines - since any cracked grains are held in place with the resin coating. Super LC uses a single curable coating that bonds with temperature or with a chemical activator (i.e. Superset). This is the lowest cost RCP and finds use in many areas and in many types of oil or gas wells.

In applications where bonding is not necessary a precured proppant can be used. A typical product for this application is called Tempered LC.

Intermediate Depths.

Because of their advantages and high long term permeability RCP's work well in both the shallow and deep parts of the gas or oil wells. The dual coated RCP such as Super DC allows the product to have pinpoint control of bond strength. This provides for fracture bonding while at the same time minimizes any bonding in the tubing or casing. The inner precured coat provides good crush resistance cold or hot, the outer curable coat provides fracture bonding which prevents flowback of the proppants, embedment, and fines migration. The coating is temperature or activator bonded.

For applications where no bonding or flowback control is necessary, precured proppants are available for intermediate depth wells. A typical product for this application is called Tempered or Tempered DC.

Deep Wells

For deeper wells having higher closure stresses and high flowback rates, dual coated RCP'provide outstanding properties which include excellent long term permeability, crush resistance, and flowback and embedment control. Super HS provides the best longterm properties. Its inner precured resin coat provides hot or cold crush resistance. Even at 16,000 psi closure stress no free fines are generated when tested at elevated temperatures. The outer curable resin coat is designed to give pinpoint control of the particle bond strength which controls flowback from the fracture, embedment and crush prevention. Super HS proppants replace low density ceramics in many deep well fracturing treatments. While cold crush test results are similar to ceramics, Super HS crushes very little when tested at actual bottomhole well conditions. All free fines or any crushed particles are held within the bonded structure.

PRODUCT COMPARISONS

Many of the available proppants are compared in Table 4 at different stress levels and in different temperature ranges. The description of each type of generic product is made and then each known company and their products are shown. This table is thought to be up to date but there may be new products not shown. While the data presented in this paper mainly pertains to Santrol's products, other data are compared when available and tested under identical conditions by an independent test lab. Figure 3 compares Jordan Sand with Super LC in the low to intermediate stress range. Clearly the curable Super LC permeability exceeds that of Figure 4 compares Super DC (dual coat) Jordan sands. permeability with AcFrac SB (single coat) and AcFrac PR (precured). At the higher stress levels the dual coat permeability exceeds the single coat and is about twice the permeability of the precured proppants. Figure 5 compares Super HS (dual coat), with low density ceramics like LWP or Carbolite which are labeled as LDISP. The low density ceramics provide a slightly higher permeability than the dual resin coat proppants; however, the lower cost and the other beneficial qualities such as cost efficiency (see below) explain why the dual resin coated materials are being substituted for the ceramics in many applications and for many different types of wells.

Long term conductivities of various proppants are sometimes used in various frac geometry or growth models. Figure 6 shows the Long Term Conductivity of various products versus Closure Stress. These test use a 2 lb/sq ft. proppant load which results in a proppant pack width of 0.2 to 0.25 inches.

CUSTOM COATED PROPPANTS

In extremely deep, high cost, or high productivity wells, dual resin coated ceramics are routinely used to provide the

best long term proppant and permeability. The dual resin coat is added to any ceramic proppant to bond in the fracture (not in tubing or casing) and to prevent flowback or fracture evacuation. Almost any material can be custom coated if the base particle can withstand the hot coat manufacturing Specialty sands, gravel pack materials, and all process. types of ceramic proppants (low density, intermediate strength, and sintered bauxite) have been coated with the dual resin coated process. Tests up to 350°F at 10,000 psi show extremely high retained long term permeability. Figure 7 shows both the conductivity and permeability of the dual resin coated ceramics conducted at an independent test laboratory with sandstone walled test cells. Even though the dual resin coated ceramic proppants are the highest cost of any available proppants, they are the best at the highest closure stresses encountered in the deeper, hotter wells.

TYPES OF WELLS WHICH USE RESIN COATED PROPPANTS

Curable resin coated proppants are not limited to any one particular type of oil or gas well. They will bond together with an activator in wells with bottomhole temperatures as low as $75^{\circ}F$. They bond together from temperature in the fracture with single or dual coated proppants when temperatures exceed $130^{\circ}F$. Sufficient bond strength to prevent flowback is attained after a given length of time based on the proppants exposure to the well's temperature. The formula used to calculate bond time is given in Equation(1).

Bond Time (hr) =
$$\frac{4 \times 10^{12}}{T^5}$$
 (1)

where T = Bottomhole temperature in degrees Fahrenheit.

Temperature range for Equation 1 is from $150^{\circ}F$ to $300^{\circ}F$ and is after fracture reheating. This equation has been found to work from field experience in water based fluids; however, in oil based fluids a rule of thumb is to double the calculated times of Equation 1. Fig. 8 shows the estimated bond time versus temperature for water and oil based frac fluids. In wells with temperatures above $190^{\circ}F$ the bond time of the resin coated proppants is less than the normal shut-in time for gel break. Wells should be brought back in a prudent manner as described in Reference 9. Besides proppant and stimulation applications, RCP's are used to provide a stable downhole filter in gravel packing and horizontal wells. These are mainly gravel packs in and around the wellbore to principally provide downhole filtering. Their ability to withstand closure stress is secondary in this application.

Some major producing areas have low temperature gradients. Even in intermediate to deep wells the bottom hole temperature is low. Many of the applications for RCP's in these areas require Superset activator (1% by volume) to provide bonding. At the other extreme in geothermal hot water wells, RCP's have been bonded thermally and used successfully to over 500°F. In the United States and South America RCP's have been used in steam injection wells to 600°F.

In the North Sea and Alaska RCP's have been used to prevent flowback and proppant evacuation in the near wellbore area. With high flow rate wells the potential for flowback is very high. In some cases, large percentages of injected ceramic proppants have flowed back to cause maintenance and disposal problems. The real problem is that the near wellbore fracture can close or narrow which may cause loss of production and severe economic consequences. Which RCP is best depends on the type of problem that is encountered with a particular well. Table 5 shows improvements seen after changing from an uncoated to a resin coated proppant.

In one field where 20 gas wells were treated, results were compared with different proppants. One of the best indicators of results is the highest gas production rate at clean-up. A higher gas rate at clean-up indicates better economics for the well. The curable and dual coated resin consistently cleaned up quicker and to higher values than sand, ceramics, or even the precured proppants used in the same field.

To summarize, RCP's have been used successfully 0 to 16,000 ft well depths. The maximum fracture closure stresses have ranged to as high as 15,000 psi while the oil and gas well bottomhole temperatures (outside of steam applications) range from $75^{\circ}F$ to $400^{\circ}F$.

COST EFFICIENCY

The rapidly expanding market for curable and dual coated proppants tells the story about well productivity results. Overall, the results are excellent particularly when side-byside comparisons are available. There are many reasons to have better results with curable or dual resin coated proppants. One measurement of how well each proppant compares is cost efficiency or the price book cost divided by the measured long term permeability.

On standard tests RCP's are found to have good long term permeability compared to other products. Figure 9 compares the cost efficiency of Santrol's product's with sand and a low density ceramic (LDISP) proppant. The lower the number on the cost efficiency graph means that you get more Darcys of permeability for each dollar spent.

The y-axis of Figure 9 is in cents/lb per Darcy of long term permeability. The cost of each proppant is taken from 1990 retail price books. The x-axis is the well's closure stress in psi. Permeability measurements in Darcies were all taken on sequential long term tests in the same comparative manner at 250°F.

The results show that sand is the most cost efficient proppant up to about 5000 psi. However, this does not consider maintenance costs, flowback problems or migrating fines. The long term permeability used here is merely the undamaged case with no fluid loss additives or pack damage. At about 5500 psi to almost 9000 psi the dual coated Super HS has the best cost efficiency. A one point long-term test not shown in Figure 9 with dual resin coating on low density ceramic gave the best cost efficiency value of 0.55 cents/lb/Darcy at 10,000 psi

CONCLUSIONS

Resin Coated Proppant (RCP) for the 1990's are effective proppants for use in hydraulic fracturing treatments of both oil and gas wells. RCP's provide the most benefit of any proppant as shown by its cost efficiency. Also these proppants provide:

- * Extra crush resistance over sand
- * Flowback protection
- * Embedment minimization
- * A locking and filtering effect on free fines and formation material
- * Inertness to acids

RCP's replace sand and ceramic particles in many applications because they perform better, longer, and bond together in the fracture.

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Table 1

Weil Depth	Closure Stress	1990's Product		
Shallow	Low	Super LC [™] (Low Cost)		
Intermediate	Medium	Super DC [™] (Dual Cost)		
Deep	High	Super HS [®] (High Strength)		

Table 2

Santrol Proppant	Closure Stress Range (psi)	Approximate Long Term Permeability (Darcy)
Super LC (Low Cost)	5000	100
Super DC (Double Coat)	7000	100
Super HS (High Strength)	9000	100

Table 3 Typical Sieve Analysis

20/40 Super HS

Sieve Size	Percent Retained	Cumulative Percent
16	0.00	0.00
20	8.40	8.40
25	60.40	68.80
30	25.20	94.00
35	4.60	98.60
40	1.20	99.80
50	0.20	100.00
Pan	0.00	100.00

20/40 Super DC

Sieve Size	Percent Retained	Cumulative Percent
16	0.00	0.00
20	5.11	5.11
25	50.23	55.34
30	38.12	93.46
35	5.10	98.56
40	1.19	99.75
50	0.25	100.00
Pan	0.00	100.00

20/40 Super LC

Sieve Size	Percent Retained	Cumulative Percent
16	0.00	0.00
20	0.42	0.42
25	4.70	5.12
30	28.45	33.57
35	44.16	77.73
40	15.61	93.34
50	6.16	- 99.50
Pan	0.50	100.00

Table 4 Proppant Reference Guide

BOTTOM HOLE TEMPERATURE	CLOSURE STRESS	DESCRIPTION OF PRODUCT	NATURAL SAND COMPANIES	SANTROL PRODUCTS	ACME	CARBO CERAMICS	NORTON
LOW 0 – 2000 psi	Angular sand, highest permeability.	Tuscaloosa Sand	n/a	n/a	n/a	n/a	
	Angular to round sand, low to medium strength.	Texas Sand, Colorado Sand, etc.	n/a	n/a	n/a	n/a	
LOW 80 - 150°F	LOW 80 - 150°F	Good to best quality round sand, fair to good strength to 4000 psi.	Texas Sand or Ottawa Sand	n/a	rı/a	n/a	n/a
100 – 6000 psi	100 – 6000 psi	Curable resin coated sand, good strength, high quality, prevents flowback.	n/a	Super LC or Super DC with Superset	AcFrac CR5000 or AcFrac CR with Activator	n/a	n/a
	Good to best quality round sand, fair to good strength to 4000 psi.	Texas Sand or Ollawa Sand	n/a	n/a	n/a	n/a	
ĺ	LOW	Curable resin coated sand, good		Super LC	AcFrac CR5000		
1	1000 – 6000 psi	gravity, prevents flowback.	rva	Super DC	AcFrac CR	n/a	n/a
		Good strength, high quality, low specific		Tempered LC	AcFrac PR5000	n/a	n/a
		gravity.	rva	Tempered DC	AcFrac PR	Carbo-Lite	LWP
	MEDIUM	Curable resin coated sand, good strength, high quality, lowest specific gravity, prevents flowback.	n/a	Super DC	AcFrac CR or AcFrac SB	n/a	n/a
130 - 225°F	5000 - 8000 psi	Good strength, high quality, low specific gravity, round proppant.	n/a	Tempered DC	AcFrac PR	Carbo-Lite	LWP
		Curable resin coaled proppant, high strength, high quality, prevents flowback.	n/a	Super DC	AcFrac SB	n/a	n/a
				Super HS	n/a		
	HIGH			Super Resin Coated Ceramic	AcFrac CR Resin Coated Ceramic		
6000 or more psi			Super HS Resin Coated Ceramic	n/a			
		High strength, high quality, round proppant.	n/a	Tempered DC	AcFrac PR	Carbo-Prop Sintered Bauxite	Interprop
MEDIUM 4000 - 7000 psi	Curable resin coated proppant, good		Super LC	AcFrac CR5000			
		strength, high quality, lowest specific	rv⁄a	Super DC	AcFrac CR or AcFrac SB	n/a	n/a
	gravity, prevents llowback.		Super HS	rı/a			
		Good to high strength, high quality, low specific gravity, round proppant.	n/a	Tempered LC	AcFrac PR5000	Carbo-Lite	LWP
HIGH 225 - 600°F 70				Tempered DC	AcFrac PR		
	HIGH 7000 or more psi	Curable resin coated proppant, high strength, high quality, prevents flowback.	n∕a	Super DC	AcFrac SB	n/a	r√a
				Super HS	n/a		
				Super Resin Coated Ceramic	AcFrac CR Resin Coated Ceramic		
				Super HS Resin Coated Ceramic	ri⁄a		
		High strength, high quality, high specific gravity, round proppant.	n/a	Tempered Resin Coaled Ceramic	AcFrac PR Resin Coated Ceramic	Carbo-Prop Sintered Bauxite	Interprop

Table 5

Previous Proppant	Replacement Proppant	Comments & Improvements
Sand	Curable single & dual coated sand	No sand fines seen or pro- duced; better long term production
Sand	Curable single & dual coated sand	No flowback of sand, better long term production, quicker clean-up
Sand or Ceramics	Curable single & dual coated sand	Embedment loss in soft or friable formations prevented
Ceramics	Dual coated sand or ceramics	No flowback of proppant, better long term production, quicker clean-up, better economics

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LONG TERM PERMEABILITY 20/40 MESH @ 250°F



Figure 4













