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Resin-Coated Proppants with Remarkably Improved Crush Resistance and Conductivity using Modified Novolac Resins

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Acknowledgements

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Resin Coated Proppant

- Base substrate coated with phenolic resin
- 4 main purposes:
 - Improved crush resistance
 - Proppant flowback prevention
 - Fines encapsulation
 - Improved conductivity
- 2 types of resin coated sands:
 - Curable: Flowback control, fines encapsulation
 - Pre-cured: Improved crush strength, fines encapsulation



Improved Crush Resistance

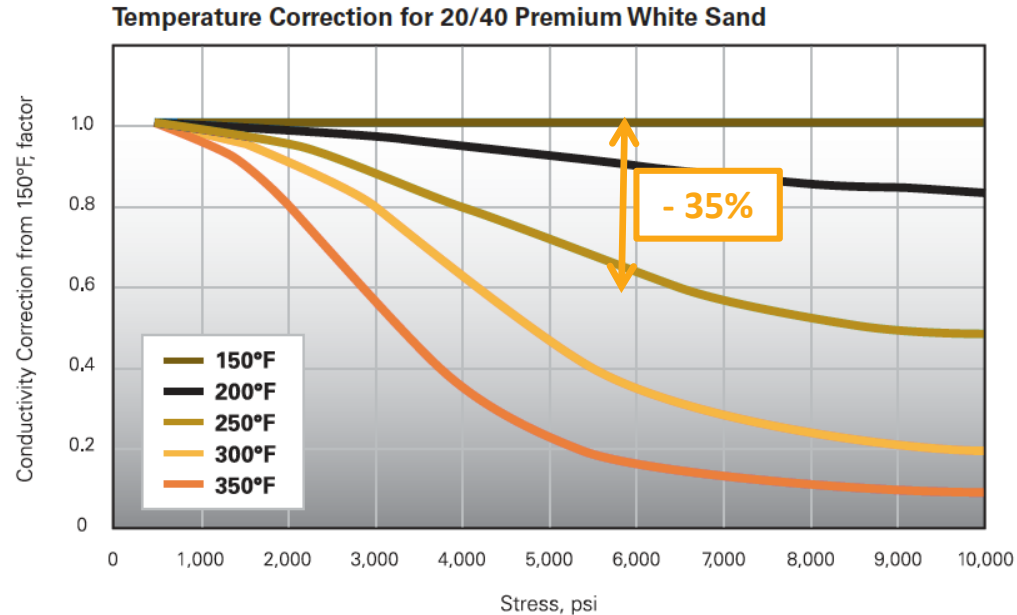
- Once the resin coating has cured, it provides increased crush strength – to both curable and pre-cured proppants
- Typical Lab Results: Crush Strength K-values:
 - 40/70 Northern White Raw: 8-10K value
 - 40/70-Curable: 14-15K value
 - 40/70-Pre-cured: >18K value



Sand loses 35% of its conductivity at 250F vs. testing at 150F while Resin Coated Proppants Do Not!

(Stim-Lab Predict-K Simulation)

AT 6000 PSI, 250°F,
20/40 WHITE SAND
**LOSES
35%**
CONDUCTIVITY
COMPARED AT 150°F



Note: Calculated corrections from Stim-Lab Predict-K.

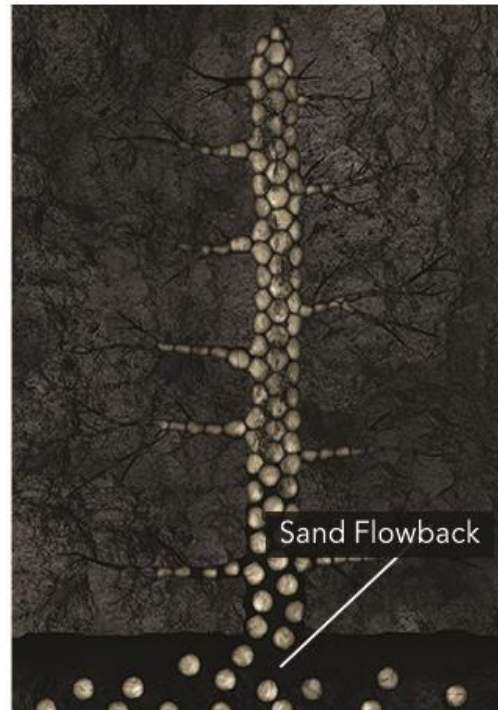
Explanation:

- 1) Sands come with a number of existing fractures present, the increase in temperature increases the reaction rate at which water, which is also present, hydrolyzes the silica at the crack tip and thus allows the crack to advance
- 2) The higher pressure of the water also contributes to this effect. It is the significant energy at the crack tip which helps drive the reaction
- 3) Crack extension leads to grain failure which lowers conductivity

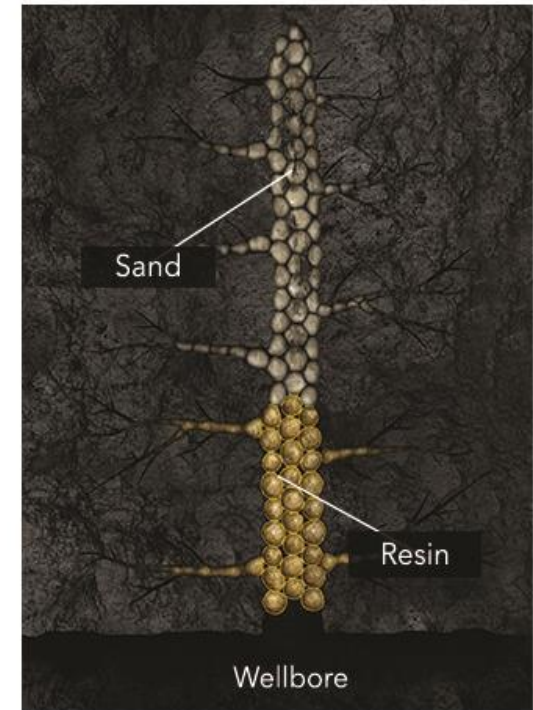
Proppant Flow Back Control

- Curable resin coated proppants
- 100% RCS use provides optimal Crush resistance and flow-back control
- Typically 20% tail-in recommended
- Resin cures with temperature under closure stress
- Grain-to-grain bonding
- Prevents proppant flowback while retaining conductivity

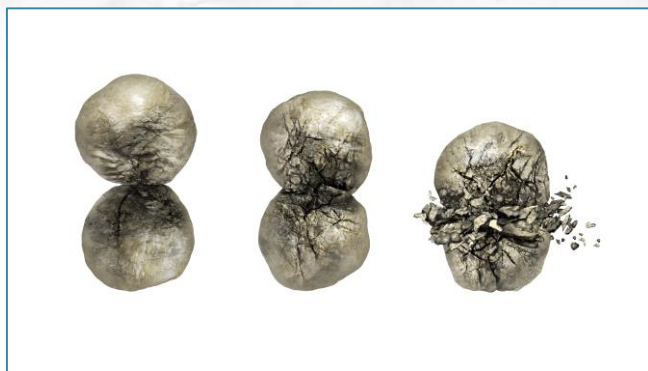
100% Raw sand



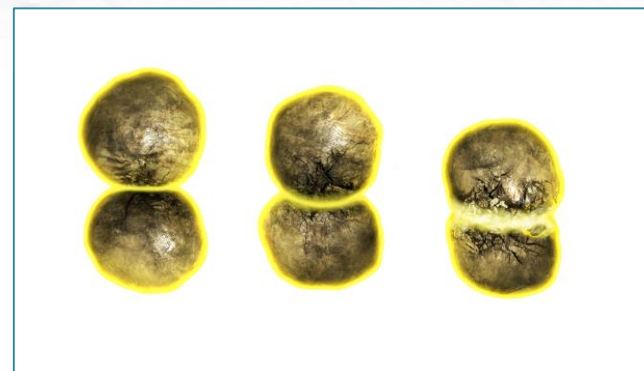
20% RCS Tail-in



Fines Encapsulation



Raw Sand Crushing



Resin Coated Sand Crushing

- Raw Sand Crushing:
 - generates fines that clog proppant pack
 - reduction in conductivity
 - decline in production
- Resin Coated Sand Crushing:
 - fines are encapsulated within the polymeric resin coating
 - Conductivity is preserved
 - Suitable for higher closure stress wells, typically above 6,000 psi

*Zoveidavianpoor & Gharibi,
Journal of Natural Gas Science and
Engineering, 2015, 24, 197-209.*

Popular Resin Systems Used in Fracking

Phenolic Novolac RCS	Polyurethane RCS
Thermoset	Thermoplastic
Stable even up to 300F	Stable up to 150-175F
Acid stable, softens above pH >10	Acid sensitive, stable to basic pH below 150F
Improves the sand crush resistance	Improves the sand crush resistance
Needs higher sand temp (>300F)	Can be coated at lower sand temperatures (200 F)
Can provide high UCS (>300 psi)	Typically UCS is <200 psi)

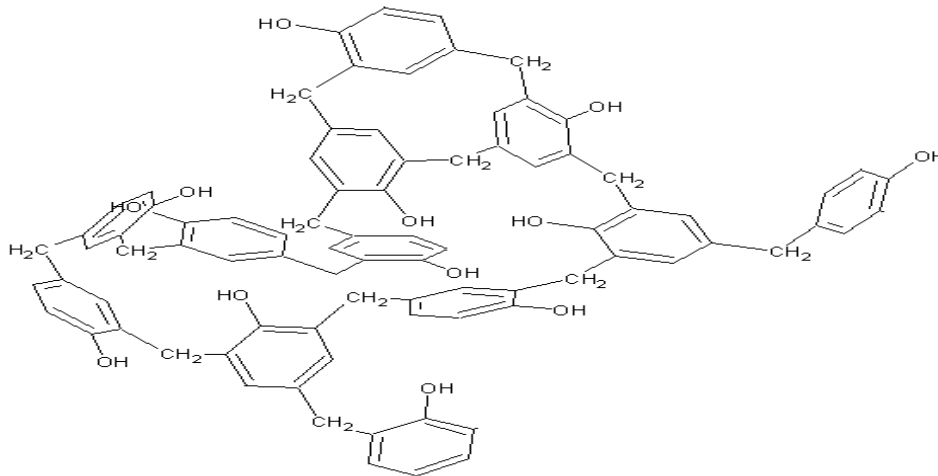
➤ Phenolic RCS products are more popular

For “Leaching studies on Novolac resin-coated proppants”, please see: Horadam, W., Venkat, N., Tran, T., Bai, L., Josyula, K., and Mehta, V. J. *Appl. Polym. Sci*, 2018, p 45845. Also, presented at ShaleTech, 2017 (Midland)

Novolac Resins for Proppant Manufacture for O & G

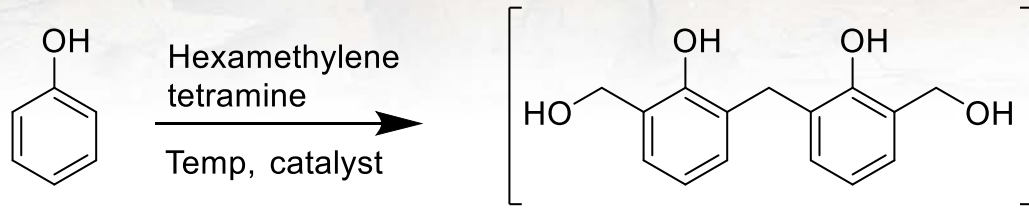
- Novolac RCPs constitute an important class of high performance proppants for O & G-eminently suited for the high temperature (250°F), high pressure (≥ 8 Kpsi) downhole environments in hydraulic fracturing operations.
- Nuances in Novolac resin molecular architecture design and sand coating processes can lead to a variety of pre-cured and curable RCPs to address a range of hydraulic fracturing requirements.

* Pilato, L. "Phenolic resins: 100 years and still going strong", *Reactive and Functional Polymers*, 2013, 73, 270-77.



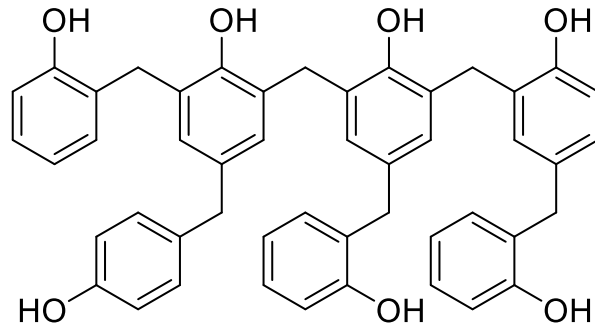
Hexamethylenetetramine
(Hexa)-Cured Novolac
Network Structure

Synthesis of Phenolic Resins



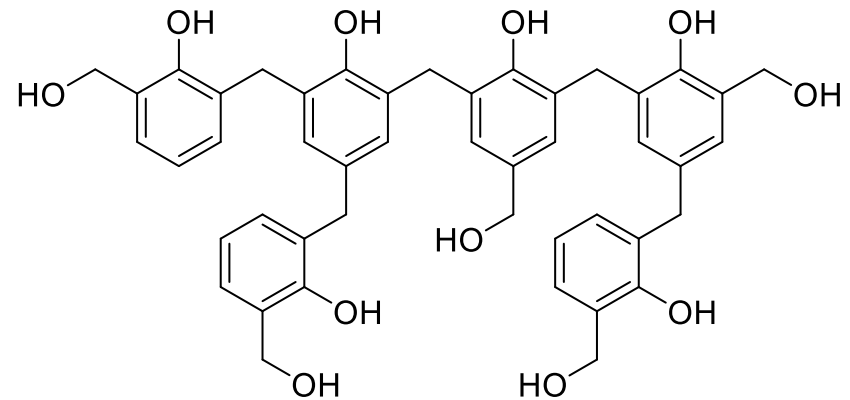
Molecular Weight: 260.29

NOVALAC



Molecular Weight: 730.86

RESOL



Molecular Weight: 774.86

➤ Can further cross-link during coating process

Factors Influencing The Crush and Conductivity of RCS

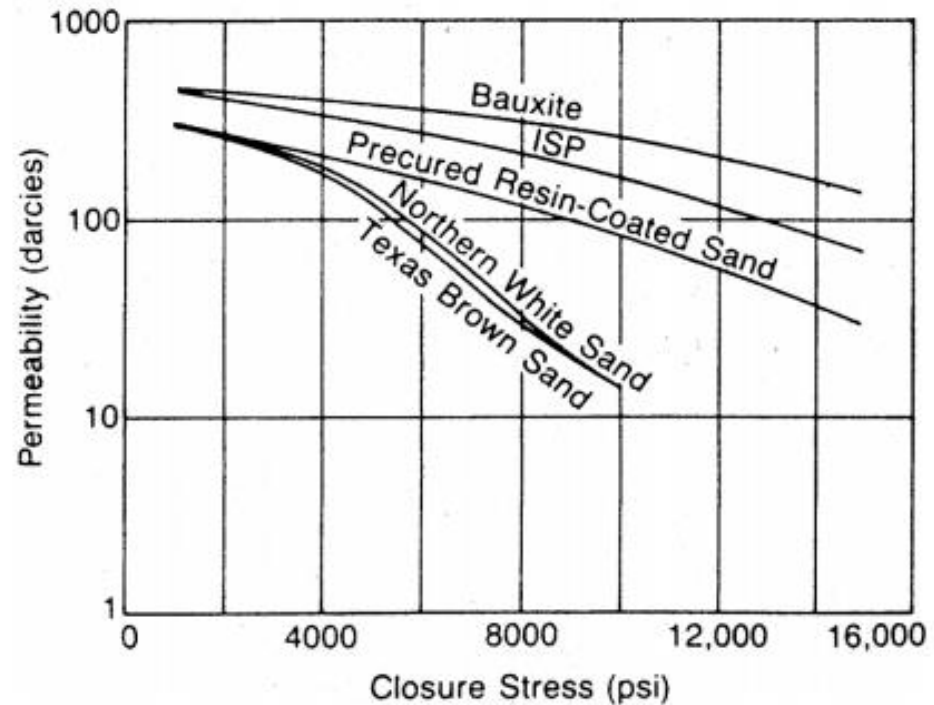
- Strength of substrate (sand quality)
- Chemistry of the resin on sand
 - Base resin: Phenolic, Polyurethane and others
 - Novel additives
- Coating process/technology
- ❖ Identified additives for superior conductivity
 - Covia proprietary technology

Requirements for Additive Screening

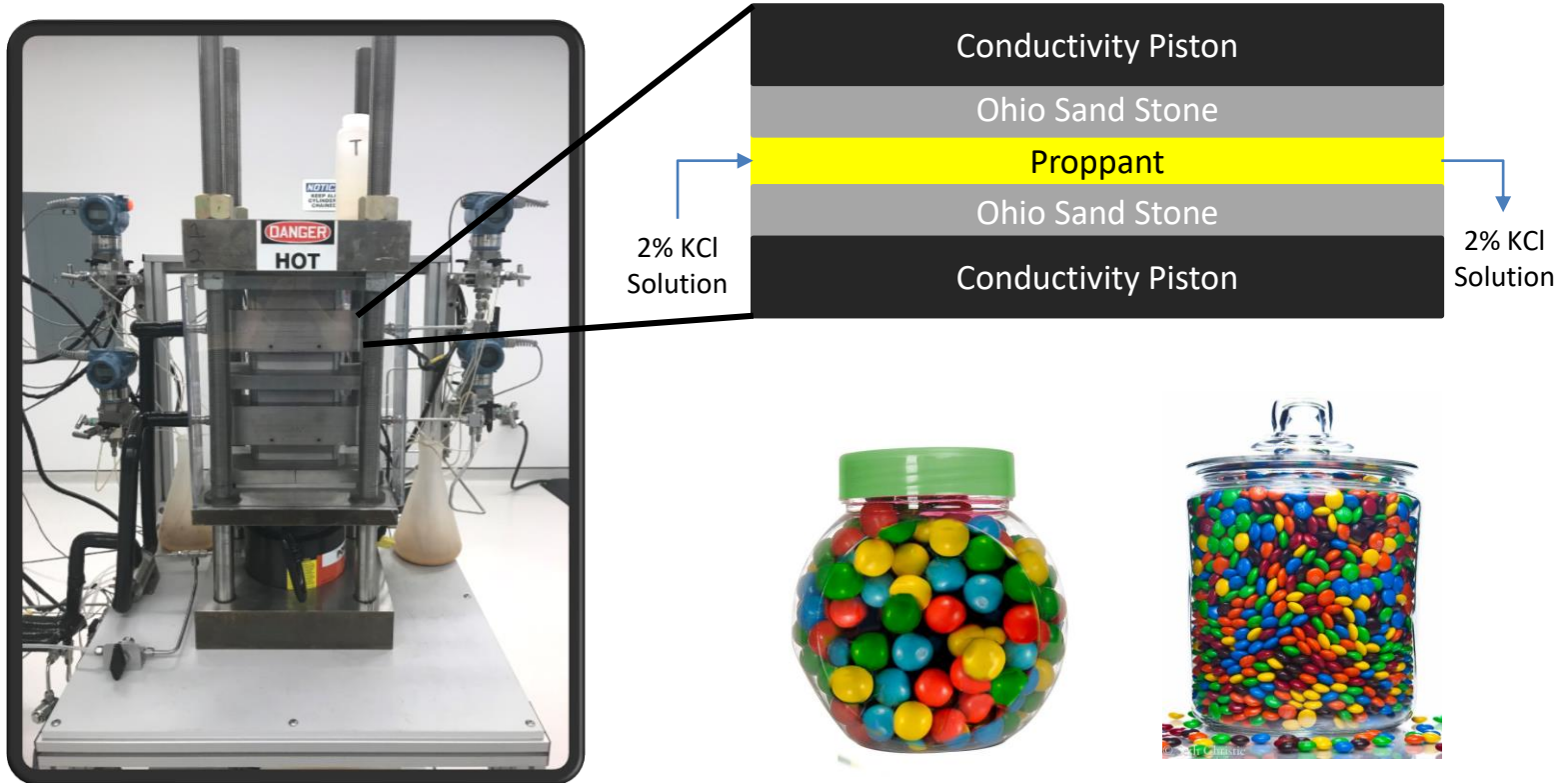
- ✓ Must be compatible with phenolic novolac resins – completely miscible, no phase separation
- ✓ Can be incorporated by simple process
- ✓ Low-cost
- ✓ No negative interactions with other fracturing operations – frac fluid compatibility

Why Resin Coating is Important?

- Proppant's ultimate goal is provide fracture **Conductivity**
- Crush Strength - Higher proppant strength to withstand higher closure pressure and avoid crushing
- Sphericity & Roundness –
 - Distribute loading and delay failure to higher closure stresses
- Turbidity – Cleanliness (fines)
- Acid solubility
- API 19 C guidelines

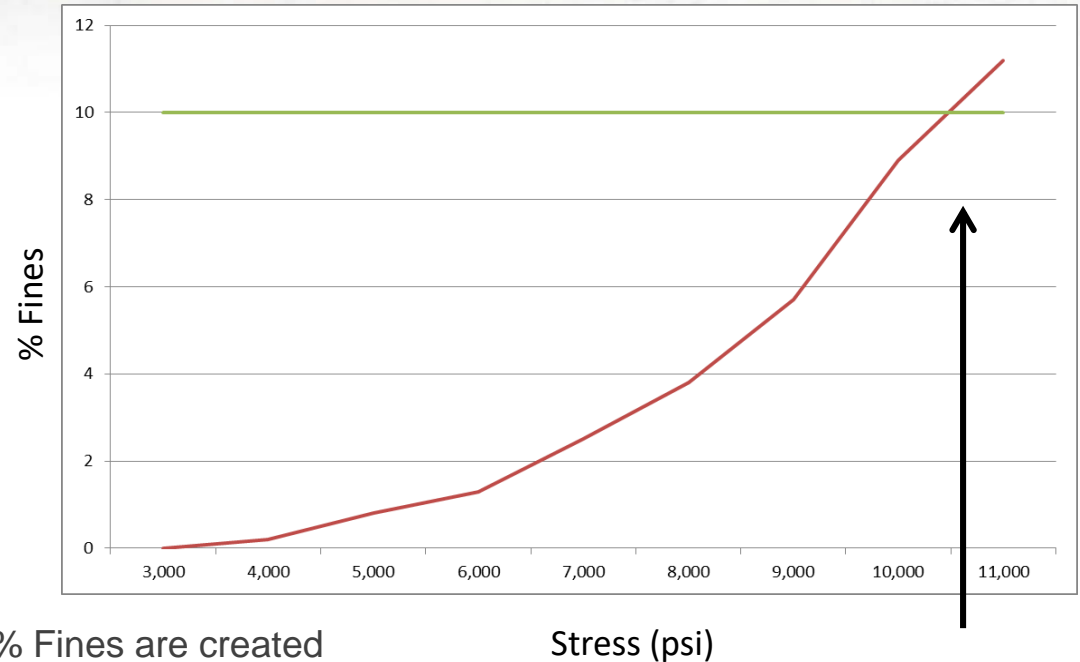


Conductivity Testing



➤ Typically done using API 19D test protocol

Crush Testing



- ▶ K value: Closure stress at which 10% Fines are created
- ▶ Used to rate the crush **resistance** of a proppant (API 19C)

Sand Type	Crush Strength (psi)
N. White Sand	6-7k
RCS-Curable	10-15k
RCS-Tempered	14-18k

For typical 20/40 grade products

Testing of Coated 20/40 RCS - Tempered

	Resin system in RCP	Crush Strength, K Value	% Conductivity Enhancement relative to RCP with base resin				
			2k	4k	6k	8k	10k
1	Base resin	14k	-----				
2	Base resin+ Additive 1	18k	-22.4%	-17.2%	-0.3%	24.9%	57.4%
3	Base resin + Additive 1 (lower level)	19k	-20.1%	-17.1%	-5.4%	13.2%	47.4%
4	Base resin + Additive 1	19k	-19.1%	-14.5%	0.1%	23.4%	57.2%
5	Base resin + Additive 2	18k	3.5%	3.5%	18.2%	27.1%	55.5%
6	Base resin + Additive 3	15k	-4.4%	-6.1%	-2.4%	2.1%	19.4%

- Several resin additives were screened, selected were presented here
- Additive 1 improved both crush and conductivity
- Based on cost and ease of use, **additive 1** selected for further studies

Additive Effect on Novalac- 40/70 RCS Tempered

	Resin system in RCP	Crush Strength, K Value	% Conductivity Enhancement relative to RCP with base resin				
			2k	4k	6k	8K	10k
1	Base resin	14k	-	-	-	-	-
2	Base resin + Additive 1	19k	-18.0%	-17.5%	-12.1%	1.4%	20.0%

- ❖ Similar crush and conductivity improvements noted for 30/50 sand grade RCS as well

Conductivity - RCS-20/40 Pre-Cured

	Resin system in RCP	Test	Crush Strength, K Value	% Conductivity Enhancement relative to RCP with base resin				
				2k	4k	6k	8k	10k
1	RCS –Pre Cured-Base	All	14k					
2	RCS-Tempered-Additive 1	Test Lab 1	18k	-20.0%	-11.3%	11.8%	35.8%	48.7%
6	RCS-Tempered-Additive 1	Test Lab 2	18k	-22.4%	-17.2%	-0.3%	24.9%	57.4%

- ❖ Conductivity testing at two different testing labs also resulted similar improvements

Batch-to-Batch Repeatability – Additive Study - 40/70 Curable

Sample (RCS)	Conductivity (Expressed as % Enhancement Over Control)				
	2k	4k	6k	8k	10k
Curable RCS Base	N/A	N/A	N/A	N/A	N/A
Curable RCS –Additive 1	-25	-14	+35	+40	+37
Curable RCS Base	N/A	N/A	N/A	N/A	N/A
Curable RCS –Additive 1	-28	-16	+32	+31	+17
Curable RCS Base	N/A	N/A	N/A	N/A	N/A
Curable RCS –Additive 1	-30	-13	+27	+46	+57
Curable RCS Base	N/A	N/A	N/A	N/A	N/A
Curable RCS –Additive 1	-10	-6	+7	+24	+29

Conclusions

- ❑ Identified additives for phenolic novolac resin systems that improve the crush strength and conductivity
- ❑ Additives are low-cost
- ❑ They can be easily incorporated into resin
- ❑ These additives are frac fluid compatible

Thank you for your attention

Questions?

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