

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

## UNITED STATES PATENT AND TRADEMARK OFFICE

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### BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

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Ex parte SAAD A. KHAN, ROBERT M. KELLY, ROBERT K. PRUD'HOMME,  
MATTHEW D. BURKE, YU CHENG and SWAPNIL CHHABRA

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Appeal No. 2005-2446  
Application No. 09/951,099

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ON BRIEF

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Before SCHEINER, ADAMS and GREEN, Administrative Patent Judges.

SCHEINER, Administrative Patent Judge.

#### DECISION ON APPEAL

This appeal involves claims to a method of “controlling the activity of thermostable enzyme breakers for the hydrolysis of polysaccharides in hydraulic fracturing fluids.” Specification, page 1. The examiner has rejected the claims as obvious over the prior art. We have jurisdiction under 35 U.S.C. § 134. We find that the examiner has not established a prima facie case of obviousness, and reverse the rejections.

#### Background

“When the pressure of oil or gas in a reservoir declines as oil or gas is taken from that reservoir, production from a well in that reservoir declines.” Specification, page 1.

“Production can be increased from such wells through oil well stimulation” which “typically involves injecting a fracturing fluid into the well bore at extremely high pressures to create fractures in the rock formation surrounding the bore.” Id., pages 1-2. The fracturing fluid contains a water-soluble polymer, which provides appropriate flow characteristics to the fluid, and also provides sufficient viscosity to suspend a non-compressible propping agent, such as sand. The purpose of the propping agent is to keep the fractures open once the pressure on the fracturing fluid is released – ideally producing a zone of high permeability. Id., page 2. However, “[w]hen [the] pressure on the fracturing fluid is released and the fracture closes around the propping agent, water is forced therefrom and the water-soluble polymer forms a compacted cake . . . [which] can prevent oil or gas flow if not removed. To solve this problem, [enzyme] ‘breakers’ are included in the fracturing fluid” to degrade the water-soluble polymer, but their effective use “requires that the onset of enzymatic hydrolysis be controlled” (id.).

“Particularly preferred [water-soluble polymers] are [ ] hydratable polysaccharides having galactose and/or mannose monosaccharide components, examples of which include the galactomannan gums, [and] guar gum[s]” (id., page 8) and the “[e]nzyme breakers are typically  $\beta$ -mannanases or  $\beta$ -glucosidases” (id., page 12). “Enzymatic attack on the polysaccharide chain can be controlled (arrested) by addition of a complexing agent . . . [such] that the enzyme is inactive or essentially inactive prior to . . . reducing the pH . . . of the fracturing fluid” (id., page 9). The complexing agent used to control the activity of the enzyme breaker may be an aminoglycol or other substituted glycol, for example, 2-amino-2-hydroxymethyl-1,3-propanediol (Tris).

In a nutshell, according to appellants, two different pH-dependent mechanisms contribute to the virtually complete inhibition of enzyme activity observed at high pH (e.g., pH 8 or 9) when the aminoglycol Tris is used as the complexing agent in the fracturing fluid. Briefly, “[w]ithout the presence of an inhibitor, [like Tris,] a simple pH change from 9 to 4 altered the relative activity of [ $\beta$ -mannanase] from 20% to 100%, based on the pH profile of the enzyme” (*id.*, pages 18 and 20). However, “an enzyme with 20% relative activity [still] produces significant [unwanted] reduction in guar viscosity” (*id.*, page 18). But Tris itself acts as a pH-dependent reversible inhibitor of  $\beta$ -mannanase, as appellants discovered when comparing the effects of two different buffers (Tris versus sodium phosphate) on enzymatic degradation of guar at pH 8 (*id.*, pages 17 and 18). “Using [Tris] inhibition in combination with a pH change, allowed [nearly complete control over] pH-activated enzyme degradation to be achieved” (*id.*, page 18), something that was not observed with sodium phosphate buffer (*id.*, page 17).

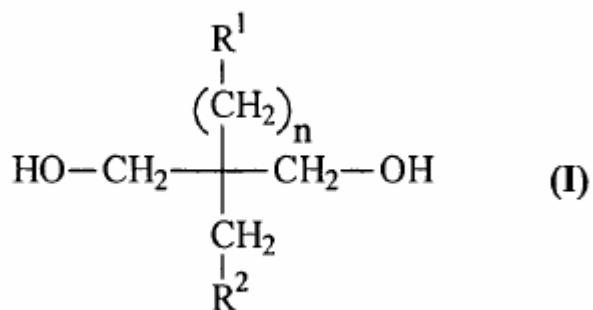
### The Claims

Claims 1-5 and 7-10 are pending and the subject of appeal. Claims 6 and 11-55 are also pending, but have been withdrawn from consideration as directed to non-elected subject matter. Additionally, in response to an election of species requirement, appellants selected 2-amino-2-hydroxymethyl-1,3-propanediol, commonly known as Tris, as the species of the compound of Formula I to be considered (Supplemental Response, October 15, 2003). It is our understanding that examination of the claims has so far been limited to that embodiment.

Claims 1-3 and 7 are representative of the subject matter on appeal:

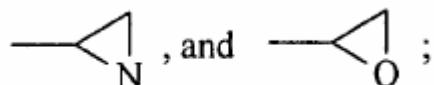
1. A method of fracturing a subterranean formation which surrounds a well bore, comprising the steps of:

(a) providing a fracturing fluid comprising (i) an aqueous liquid; (ii) a polysaccharide soluble or dispersible in said aqueous liquid in an amount sufficient to increase the viscosity of said aqueous liquid; (iii) an enzyme breaker which degrades said polysaccharide; and (iv) a compound according to **Formula I** in an amount sufficient to reduce the polysaccharide-degrading activity of said enzyme breaker;



wherein:

$\text{R}^1$  is selected from the group consisting of: -F, -NR<sup>3</sup>R<sup>4</sup> wherein R<sup>3</sup> and R<sup>4</sup> are each independently selected from the group consisting of H, loweralkyl,



$\text{R}^2$  is selected from the group consisting of -H and -OH; and n is 0 to 3;

then;

(b) injecting said fracturing fluid into said well bore at a pressure sufficient to form fractures in the subterranean formation which surrounds said well bore; then

(c) reducing the pH of said fracturing fluid by an amount sufficient to increase the polysaccharide-degrading activity of said enzyme; and then

(d) releasing the pressure from said fracturing fluid.

2. A method according to claim 1, wherein said enzyme is a  $\beta$ -mannanase.

3. A method according to claim 1, wherein said enzyme is a  $\beta$ -glucosidase.

7. A method according to claim 1, wherein said compound of Formula I is 2-amino-2-hydroxymethyl-1,3-propanediol.

### Discussion

The examiner rejected claims 1, 3-5 and 7-10 under 35 U.S.C. § 103 as unpatentable over Dawson<sup>1</sup> in view of Segel.<sup>2</sup> In addition, the examiner rejected claims 1-5 and 7-10 under 35 U.S.C. § 103 as unpatentable over Dawson and Segel, and further in view of Christgau.<sup>3</sup> Because we consider the examiner's proposed combination of Dawson and Segel to be central to both rejections, we will discuss the rejections together.

Dawson describes "a gellable fracturing fluid [ ] formulated by blending together an aqueous fluid, a hydratable polymer, a suitable crosslinking agent . . . and an enzyme breaker which is effective to degrade the polymer gel at temperatures below about 140-150 F within a time period less than about 24 hours. In order to provide a controlled break, the pH of the fracturing fluid is initially raised above about 9.0, whereby the enzyme breaker is inert. A pH regulating substance is also incorporated in the fracturing fluid which slowly hydrolyzes to produce a Bronsted acid, thereby dropping the pH of the fracturing fluid. As the pH . . . drops, the enzyme breaker is activated to attack the polymer" (Dawson, column 2, line 56 to column 3, line 2). "Propping agents are typically added to the base fluid prior to addition of the crosslinking agent" (*id.*, column 4, lines 52-54).

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<sup>1</sup> Dawson, U.S. Patent 5,067,566, issued November 26, 1991.

<sup>2</sup> Segel, I.H., in Biochemical Calculations, John Wiley & Sons, New York, Appendix IV, pp. 403-406 (1976).

<sup>3</sup> Christgau et al., U.S. Patent 5,795,764, issued August 18, 1998.

According to Dawson, “suitable hydratable polysaccharides are the galactomannan gums, glucomannan gums, guars, derived guars and cellulose derivatives” (id., column 3, lines 21-24). “Suitable enzyme breakers include, for example, the cellulases . . . [which] specific[ally] [ ] degrade the particular polymeric linkage found on the polysaccharide polymer backbone of the crosslinked gel, for instance, the 1,4 linkage between mannose in galactomannans” (id., column 4, lines 11-21). Finally, according to Dawson, “[a]ny conventional buffer can be used to adjust the pH, for instance aqueous potassium carbonate” (id., column 5, lines 1-2).

The examiner acknowledges that “Dawson differs from the claims in not disclosing the use of . . . ‘Tris’[ ] as the buffer in the [alkaline] pH adjustment step” (Examiner’s Answer, page 4), but relies on Segel’s list of “acids and bases that are useful in preparing buffers for enzyme assays” as evidence that “Tris is an extremely well known buffer, conventionally used in processes employing enzymes” (id.). Moreover, the examiner notes that Tris “has an alkaline pKa of 8.1 and is therefore capable of providing buffering power in the alkaline range initially required in Dawson’s fracturing fluid” (id.).<sup>4</sup> According to the examiner, “the artisan of ordinary skill clearly would have recognized Tris as being a conventional buffer suitable for processes employing enzymes, [thus,] the claimed substitution of Tris into Dawson’s process must be . . . considered obvious” (id., pages 4 and 5).

Appellants argue that the examiner’s conclusion is unfounded because, among other things, “[t]he only specific reference to Tris buffer systems having a particular pH in

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<sup>4</sup> We note that the pK<sub>a</sub> value provided here is for Tris at 25°.

Segel [ ] is the statement . . . that malic acid and Tris can be mixed to produce Tris-maleate buffers of pH 5.7 to 8.6 . . . and the upper end of this range is substantially below the ‘about 9.0’ minimum required in Dawson (indeed, the specific examples of Dawson suggest a still higher pH is required)” (Brief, page 4).

“In rejecting claims under 35 U.S.C. § 103, the examiner bears the initial burden of presenting a prima facie case of obviousness. Only if that burden is met, does the burden of coming forward with evidence or argument shift to the applicant.” In re Rijckaert, 9 F.3d 1531, 1532, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). “[I]dentification in the prior art of each individual part claimed is insufficient to defeat patentability of the whole claimed invention. Rather, to establish obviousness based on a combination of the elements disclosed in the prior art, there must be some motivation, suggestion or teaching of the desirability of making the specific combination that was made by the applicant.” In re Kotzab, 217 F.3d 1365, 1369-70, 55 USPQ2d 1313, 1316 (Fed. Cir. 2000).

On reflection, we agree with appellants that the cited references, viewed without the benefit of hindsight, would not have suggested the claimed method to a person of ordinary skill in the art. Quite simply, while we would agree with the examiner that Tris is a well known and conventional component of buffers used in enzyme assays, we see nothing in the evidence provided that would suggest the conventional use of Tris at pH 9.0 or above, where Dawson’s enzyme breakers would be inactive. While we would not go so far as to agree with appellants “that the references, when considered as a whole, teach away from the proposed combination” (Brief, page 5), neither do we find anything in Dawson and Segel that particularly suggests the specific combination made by

appellants. Christgau, cited by the examiner as evidence that the  $\beta$ -mannanase required by claim 2, "is particularly suited as a breaker for use in guar-containing fracturing fluids" (Answer, page 5), does nothing to remedy this deficiency.

We find that the examiner has not established a prima facie case of obviousness for the claimed invention. Accordingly, both rejections of the claims under 35 U.S.C. § 103 are reversed.

REVERSED

Toni R. Scheiner	)
Administrative Patent Judge	)
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	)
	)
	) BOARD OF PATENT
Donald E. Adams	)
Administrative Patent Judge	) APPEALS AND
	)
	) INTERFERENCES
	)
Lora M. Green	)
Administrative Patent Judge	)

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