Memo: 8/27/97 from Dan Joseph

To: Simon Suarez, Mayela Rivero, José Guitián, Ignacio Layrisse, Gustavo Núñez

Patent for shaker bottle

I want to bring your attention to some applications of shaker bottles which appear to be of interest in the study of foams.

1. We already discussed the possibility of using a shaker bottle to know how much surfactant to add to restore a used foam. You put in the new surfactant and the water from the collapsed foam in a certain given volume and shake up the mixture. The mixture will foam and when it reaches a certain level marked on the bottle, just the right amount of surfactant has been added. José knows about this; it couldn't be easier.
2. The shaker bottle method for adding chemicals to restore degraded foams is apparently particularly appropriate for pH controlled foams being used by Maraven and Baker Hughes. This foam was invented and patented by Todd Thomas of Clearwater Inc. There are two patents, 5,385,206 and 5,591,701. The second patent specifies the chemicals, acid to restore foams, caustic to break foam. Here are some excerpts from patent 5,591,701:

> **Abstract.** In the removal of particulates from a wellbore, such as in air drilling for hydrocarbon recovery, a mixture of an amphoteric foaming agent and, typically, an anionic surfactant is employed. An aqueous solution thereof having a pH of at least 9.5 is used to generate a foam for removing the particulates; then the foam is collapsed by the introduction of acid to reduce the pH below about 4, the particles are removed mechanically, the pH is restored to greater than 9.5, and the foaming solution is returned to the wellbore. The solution may be used several times; partial losses of foaming agent in the process may be easily replenished with each cycle. Cationic surfactants may be used instead of anionic, with foaming and foam collapse being controlled at opposite pH's. Savings are realized in water, drilling chemicals, and settling pits and the like for removing particulates from the foam.
>
> For air foam drilling, my two-component foaming composition should be used in concentrations of about 0.2% to about 0.4%, and preferably about 0.4% to about 0.7% by weight based on the solution without considering the weight of the particulates. Any of the anionic foamers (surfactants) known in the art to be useful as foaming agents in well cleanup or air drilling may be used in my process. See the examples described in the above cited Rogers, Tillotson, and Lissant patents, for example. Conversely, I may employ cationic surfactants which will foam in combination with amphoterics at pH's below about 3.5 and which will collapse at about pH 9.5. When employing such combinations of materials,

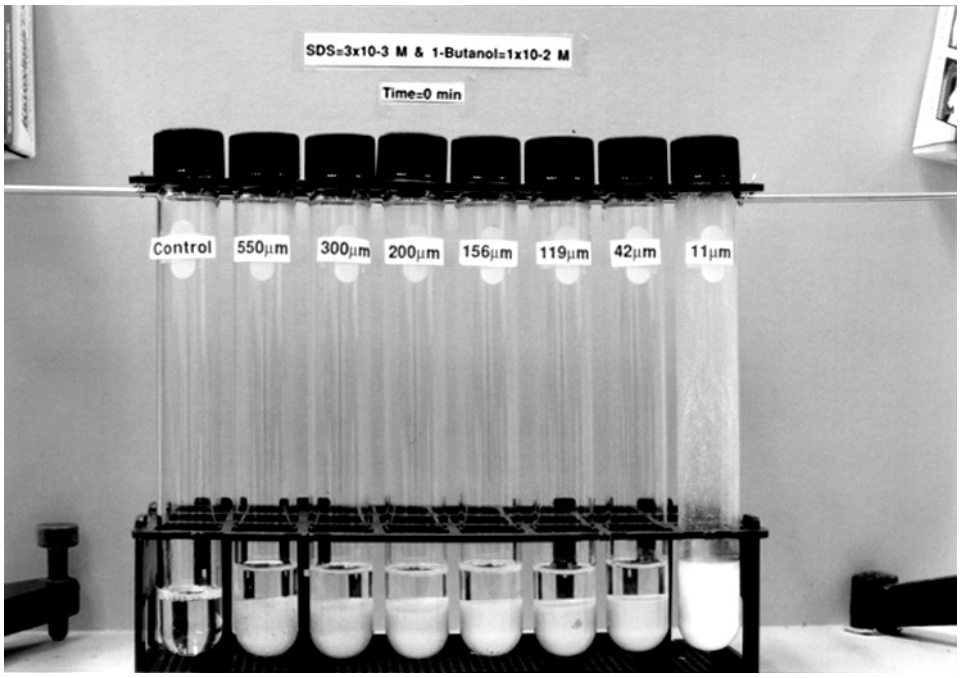
> I use caustic materials to collapse the foam, and add acid to cause the foam to form again.
>
> I have found the several iterations of the foam cycle may be employed without losing the efficiency of the process, although, since some of the surfactant is necessarily left with the solids removed at the wellhead, replenishment to at least some extent is usually necessary with each iteration. I have found that, if one is to continue the use of a composition similar to the one used in the beginning of the process, the solution used for replenishing the surfactants with each cycle should have a molar ratio of anionic to amphoteric of about the same, preferably 0.6:1 to about 1.4:1.

I talked to Thomas and I know that his recipe for restoring the foam by adding acid is a rule of thumb. We could do better with shaker bottles.

Shaker bottles are also good for testing stability of foams. Raal found that a little hydrocarbon destroys Clearwater's foam, but Thomas says that some of his formulations are stable with high fraction (70%) hydrocarbon. Maybe the shaker bottle can be used to test the stability of pH controlled aqueous foams with different hydrocarbon fractions.

3. My student Ling Jiang has used shaker bottles to test stability of foams when particles are present. She did one test with different size particles. Small and large particles fall out of the foam. Intermediate size particles do not fall out. There is an optimal size for which the solids fraction of particles stuck in foam to the total volume of particles (fixed and the same for all tests). So a given size cutting will be effectively removed by a foam drilling mud, with removal of other sizes being less good (see Figure 1). She wrote a report on her work which I am going to send to José.

(a)



(b)

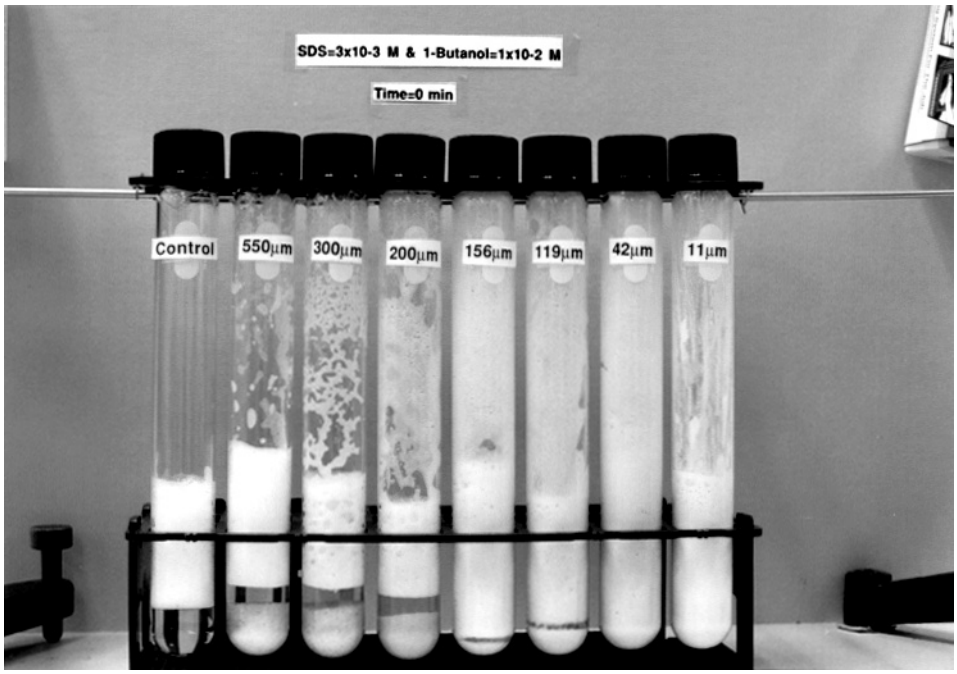
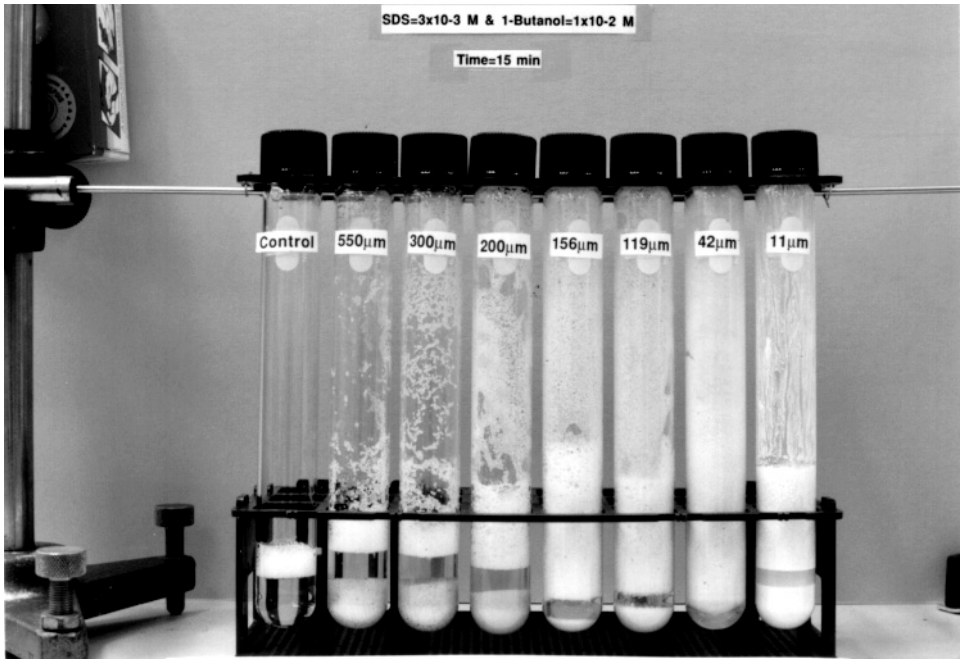


Figure 1 *(continues, next two pages)*. 10 gms of glass of different sizes marked on the bottles are put in 7cc of surfactant solution (a) before shaking, (b) just after shaking, (c) 15 min. later, (d) 30 min. later, (e) 1 hour later. The optimal size of cutting for this foam is d = 156 mm.

(c)



(d)

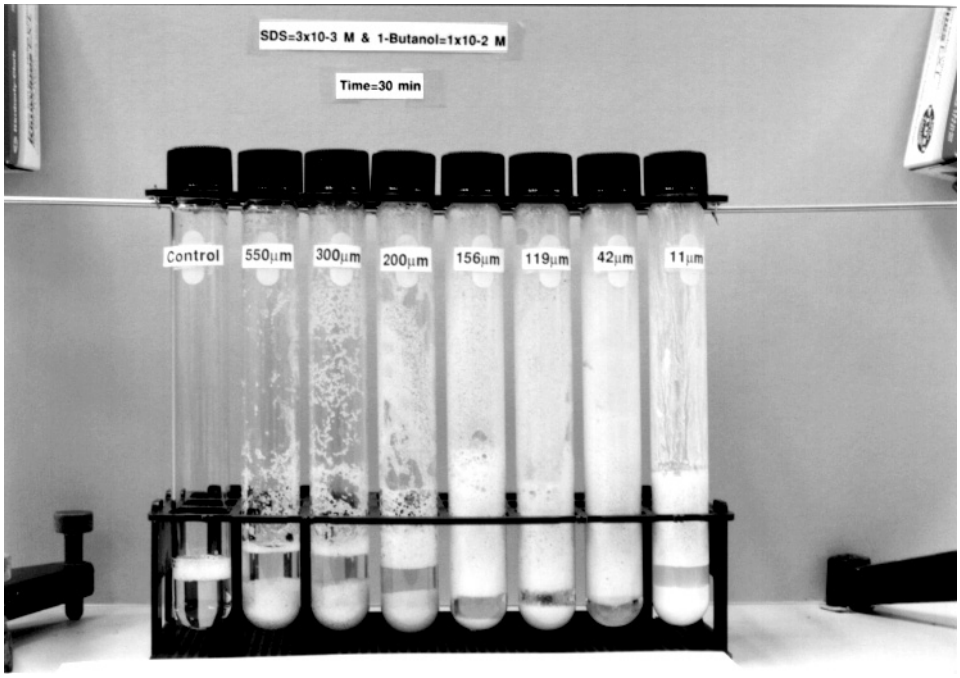


Figure 1, *cont.*

(e)

Figure 1, *cont.*

4. So far Shell wants to get us support under the Global Petroleum Research Institute (GPRI) to study surface foaming of hydrocarbons of crude oils from the Gulf. Their oils are lighter than ours. Bob Chin, my sponsor at Shell told me that their main goal was to be able to distinguish the foaminess and stability of different foamy oils with a simple test (maybe for workers on drilling rigs). I didn't tell him to try shaker bottles as I eventually will. He is going to send me samples of his crude oils and we will see if we can use shaker bottles to study them. I thought that we might consider getting an Intevep patent for shaker bottles with the foregoing as our set of claims.