Estd. 1989
Asian Journal of Chemistry

Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5453-5456

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18130

Fire Resistance of Three-Phase Foam with Modified Hollow Glass Microspheres†

BAOHUA TANG[1,2,*]

[1]Fundamental Department, The Armed Police Academy, Langfang, Hebei, P.R. China
[2]School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, P.R. China

*Corresponding author: E-mail: ztbh@sina.com

AJC-15720

In this work, fluoroalkylsilane [F_3C-$(CF_2)_5$-$(CH_2)_2$-$Si(OC_2H_5)_3$, F-8261] was used as surface modifier for oleophobic hollow glass microspheres. Then three-phase foam was prepared with the modified oleophobic hollow microspheres. The results showed that the stability and antiburning properties of three-phase foam on oil were improved significantly. The optimum results were achieved with the addition of 12 % of fire fighting protein, 50 % of hollow microspheres and 0.5 % of F-8261.

Keywords: Silane coupling agents containing fluoride, Hollow glass microsphere, Three-phase foam, Ability of antisolubility.

INTRODUCTION

With the rapid economical development, the demand of oil has been increasing consistently in China. Oil tanks are the most common equipment for bulk oil storage and transportation. In an event of fire, large quantities of flammable oil would combust intensely, resulting in extreme difficulty in fire control. As a most common type of fire extinguishing agent and to save bulk oil, fire foams are often used to control and put out fire, which can isolate heat transfer to oil surface and restrain oil evaporation. During a fire-fighting process, the effectiveness of fire foam depends on two main aspects *i.e.*, the capacities of fire resistance and oil repellence. If the foam is burned, it cannot cover the oil surface completely, then the oil surface temperature will be high and the fire cannot be under control. If the foam does not have strong oil repellence, it will be invaded by oil easily. When the foam's gravity exceeds its critical carrying capacity, the foam height decreases quickly and the accelerated fracture can deteriorate the foam's stability and antiburning property on the oil surface[1-8].

As a kind of particle material developed in the 1950s and 1960s, hollow glass microspheres have many advantages such as low density, low thermal conductivity, low oil absorption rate, high temperature resistance, good thermal stability, corrosion resistance, controllable particle size and chemical composition, *etc*. In this work, hollow glass microspheres were added into fire foams to overcome the foam's shortcoming of instability. By modifying the hollow glass microspheres surface, the stable three-phase foam demonstrated strengthened oil repellence and some significant enhancement was achieved.

EXPERIMENTAL

Electric mixer (JJ-1 type, speed 200-3000 rpm, 30 cm × 35 cm × 76 cm) and isothermal stirrer were purchased from Jintan Guosheng Experimental Instrument Factory (Jintan, Jiangsu). Thermometer (XM T-type digital display regulator) was from Yuyao City's Second Industrial Instrument Plant. Radiation heating apparatus (power 300W, SLT-181TX type) was from Shenzhen Instrument Factory.

During the experiment, an ultrasonic cleaner (sk3310LHC), a 400 mL beaker, several 200 mL beakers and a stopwatch were used.

Hollow glass microspheres were obtained from Qinhuangdao Auge Glass Microspheres Company. The microspheres' size ranged from 10-100 μm, the bulk density was from 0.18-0.20 g/cm^3, the floating rate was higher than 93 % and the crushing density was from 3-5 MPa.

F8261, short for tridecafluorooctyltriethoxysilane [F_3C-$(CF_2)_5$-$(CH_2)_2$-$Si(OC_2H_5)_3$], was purchased from Wuhan Defu Economic Development Co., Ltd. General fire protein foam liquid, with the quality meeting the technical requirements of ZBC84007, was provided by Pharmaceutical Plant of the Armed Police Academy.

Kerosene and gasoline were provided by the Fire-fighting Engineering Laboratory of the Armed Police Academy.

---

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

Surface modification of hollow glass microspheres and foam's fire-resistant experiment: Firstly, hollow glass microspheres were cleaned by mixed solution of concentrated sulfuric acid and hydrogen peroxide solution (ratio 7:3) with ultrasound for 45 min. Then the microspheres were filtered, placed in a mixture of ammonia, hydrogen peroxide and water (ratio 1:1:5) and stirred for 4 h at room temperature. Later, the microspheres were reserved by suction filtration and dried for 24 h.

The pH of ethanol solution was adjusted to below 3 by concentrated hydrochloric acid and a certain amount of F8261 was added in. Then the pre-treated hollow glass microspheres were put in the mixture for surface modification with ultrasound for 45 min. Finally, the mixture was stirred for 6 h, the microspheres were filtered, dried for 24 h and placed in oven for use.

The protein foam liquid was mixed with certain amount of hollow glass microspheres. In a 400 mL beaker, the protein fire foam liquid of 6, 8, 10, 12 mL, respectively was diluted to 100 mL by adding water. The solution was stirred by the electric mixer and then the height of generated foam was measured. The foam was placed in a heat wave transmitter immediately, while the temperature of the heat source was maintained at about 320 ºC. When the air temperature on the foam surface was increased up to 280 ºC, the foam's height and the height change of bottom liquid in the beaker was recorded with the baking time. The foam's shape was also observed as the time progressing.

On the other hand, a certain amount of hollow glass microspheres were added into the protein foam liquid and then the foam was stirred rapidly under the thermal radiation heating device. The beaker's top was placed 2 cm away from the radiant heating panel. The foam's height change with time was recorded in the condition of thermal radiation. The effect of microspheres' addition on the thermal stability of the foam was studied.

Determination of foam's properties: Referring to the application of "Fire Foams General Technique Requirements GB15308-94", the foam's properties were characterized including the 25 % drainage time, the oil surface stability and sealing performance.

RESULTS AND DISCUSSION

Effect of foam concentration on foaming and fire-resistant capacity: For the foam with low concentration of the protein fire foam liquid, the heat resistance decreased significantly, while the foam's height changed rapidly as time passes. The surface of low concentration foams seemed collapse-like, as shown in Fig. 1. In contrast, for the foam with high concentration, when the baking came to later stage, a layer shell was formed which had heat insulation effect. When the time passes, the foams' decline rate reduced, which might have two reasons. First, since the height of the heat wave transmitter was fixed, with the decrease of foams' height, the baking temperature on the foams' surface decreased. Specifically, when the heating time was 14.5 min, the temperature on the foams' surface dropped to 140 ºC and the distance between the heat source and the foam surface was 7.3 cm which was 2 cm originally. Second, after having been heated, the foam's surface deteriorated and formed a layer shell which had heat protection effect.

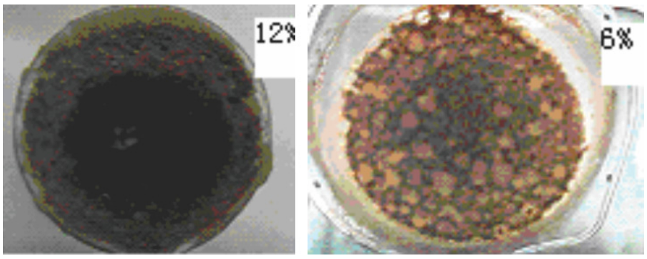

Fig. 1. Morphology of 12 and 6 % foams after baking

Fig. 2 shows the effect of foam concentration on foaming and fire-resistant capacity. As can be seen, under certain heat radiation conditions, the foam with 12 % of protein foam liquid had the least height change over time. The antiburn performance can be ranked with the concentration as 12 % > 10 % > 8 % > 6 %. Therefore, with 12 mL of protein foam liquid, the foam's antiburning property was the best.

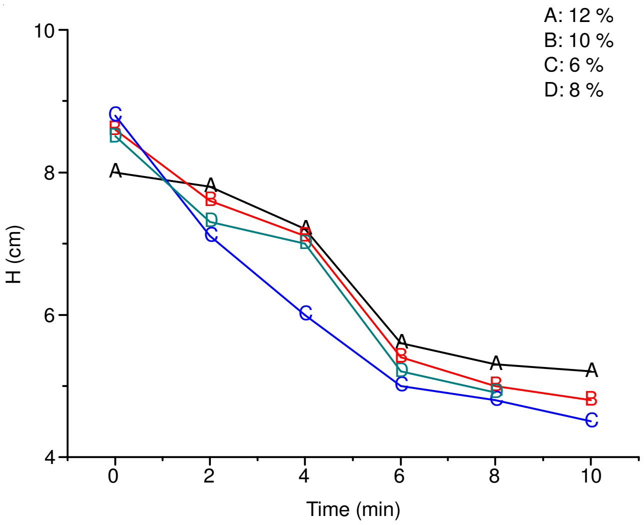

Fig. 2. Effect of foam concentration on foaming and fire-resistant property

Effect of the surface activity agent on foaming and fire-resistant property: The stability of liquid film depends on the process of foaming and defoaming. As a foaming agent has high surface activity, it can effectively reduce the surface tension thereby to form an elastic membrane on the foams' surface and improve the foams' stability which would not be easily broken under normal conditions. In our study, 2 mL of 1 % diluted fluorocarbon surface activity agent was added to the foam and the morphology of the generated foams was observed (Fig. 3). Compared with the foams without the surface activity agent, the foams with agent appeared much smoother and there was little change of the foams' height. After being exposed to high temperature, the surface shell became black and hard-packed, while the height change of bottom liquid in the beaker was little. Therefore, the foam with the surface activity agent had good water holding capacity and antiburning property.

Effect of hollow glass microspheres: Fig. 4 shows that the addition of hollow glass microspheres had significant impact on the fire-resistant property of foams. With 50 mL of hollow glass microspheres, the foam displayed the strongest antiburning property. After being heated for 5 min, the foam's

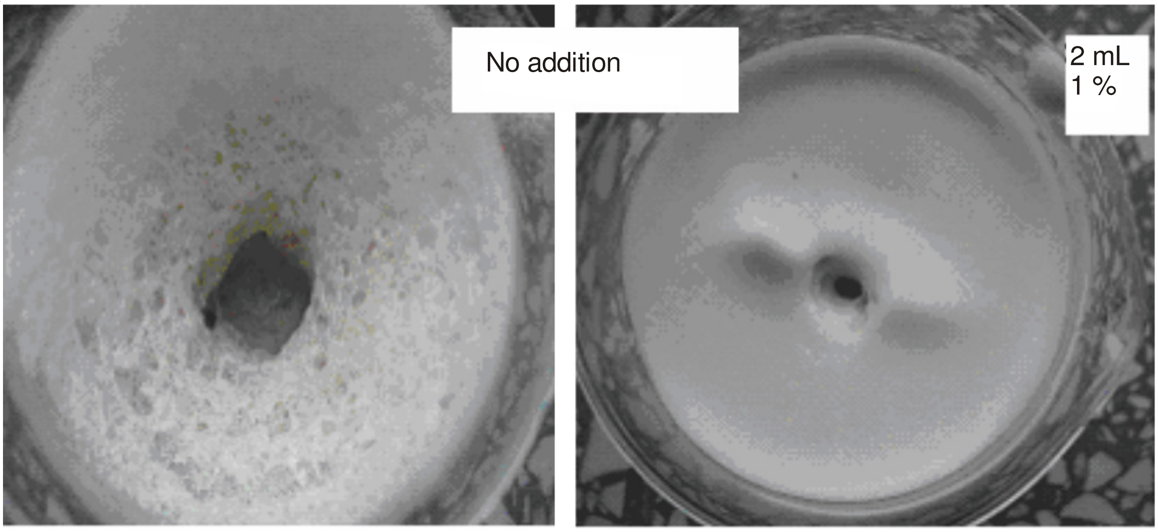

Fig. 3. Effect of fluorocarbon surface activity agent on the foam's morphology

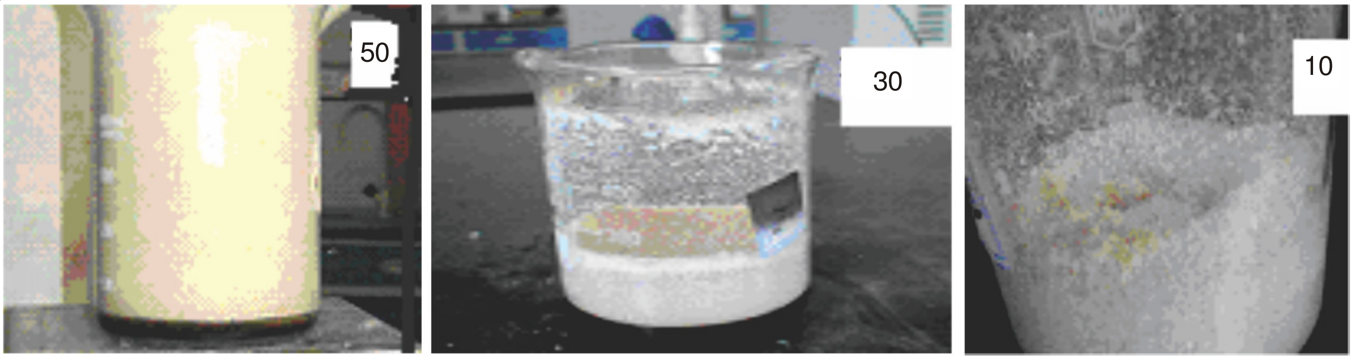

Fig. 4. Comparison of the morphology of the foams with different amount of hollow glass microspheres after burning for 10 min

height did not change and a dense shell coating was formed on the surface. The sample with 30 mL of microspheres was also able to form a shell on the surface, but the foam's height decreased rapidly. For the foam with only 10 mL of microspheres, no hard shell coating can be formed. The foam structure was loose with surface subsidence and its antiburning property was poor. If too many hollow glass microspheres were added, foaming was not easy for the solution. So the optimum amount of microspheres was 50 mL. Under this condition, the pore size in the foam was relatively small and the height of bottom liquid in the beaker rose slowly, resulting in the best fire-resistant property.

Determination of foam property

Determination of 25 % drainage time: In the experiment, 100 g of three-phase foam with the bottom liquid was placed in a container, which was put on a digital scale (range 0-3000 g, precision ± 0.01 g). The temperature's change of the foam solution was neglectable, so it had little effect on the liquid viscosity. Fig. 5 showed the modified powder was better than the unmodified and adding a certain amount of surface activity agent could increase the drainage time.

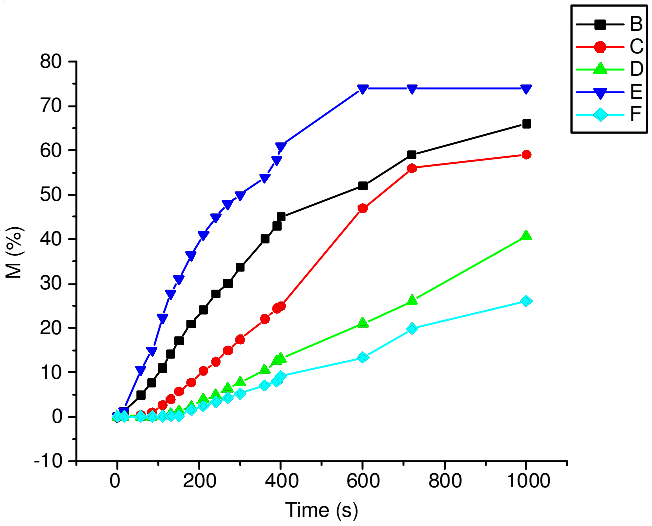

Fig. 5. Effect of FC and hollow glass microspheres on 25 % drainage time of foams. B:12 % + 88 mL water, C: 12 % + 88 mL water + 30 mL powder + FC, D: 12 % + 88 mL water + 30 mL modified powder + 2 mL FC, E: 12 % + 88 mL water + 30 mL powder, F: 12 % + 88 mL water + 30 mL modified (coarse) flour + 2 mL FC

Comparison of the foam stability on oil surface: The experimental setup for the foam's antisolubility test is illustrated in Fig. 6. 100 mL of 12 % foam mixed liquid and 20 mL of hollow glass microspheres were added into a 500 mL beaker. After being mixed and stirred at high speed, three-phase foam would be obtained. Then 25 mL of No. 93 gasoline was injected at the foams' bottom. During the experiment, the stirring speed, stirring time, injection location and injection

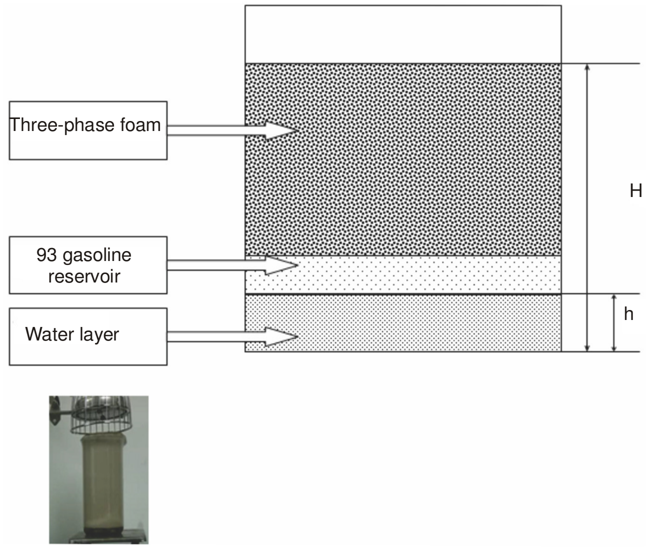

Fig. 6. Test diagram of three-phase foam's stability on the oil surface

rate of oil products were well controlled. For the foams with normal protein, with hollow glass microspheres and with modified hollow glass microspheres, the changing of oil thickness was recorded with time. The stability of different foams was shown in Fig. 7.

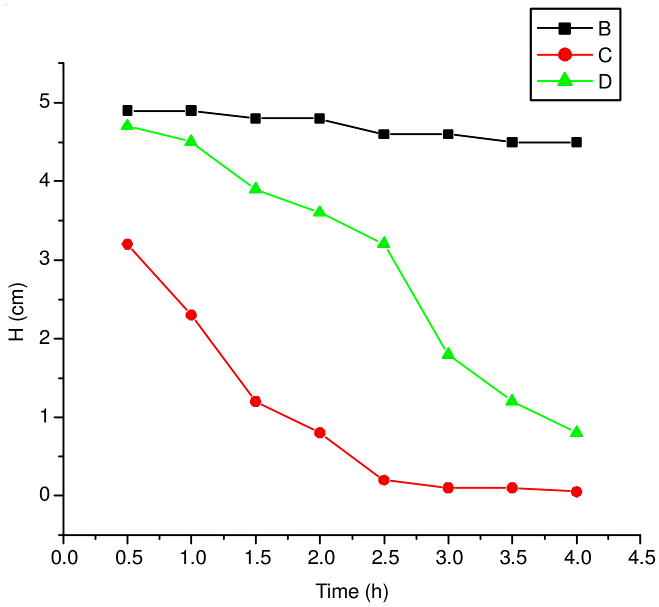

Fig. 7. Comparison of foam's stability on the oil surface (B. with modified hollow glass microspheres; C. with unmodified hollow glass microspheres; D. with general protein)

Conclusion

In this study, comprehensive investigation was performed on the effects of hollow glass microspheres, surface modification, surface active agent and other factors on the three-phase foam's stability and fire-resistance. It was found that, to achieve the best properties, the optimum reaction conditions were 12 % of fire fighting protein with the addition of 50 % of hollow glass microspheres and 0.5 % of F-8261. As a result, the foam's properties were enhanced significantly. Nevertheless, all the modification conditions were the test results in a laboratory, which need to be further validated by amplified experiments. Besides, only a few modification reagents were discussed in this work. In the future, more other reagents can be examined to realize surface treatment with better properties, simpler process and lower cost.

ACKNOWLEDGEMENTS

This work was financially supported by the Application and Innovation Project of Ministry of Public Security (No. 2013YYCXWJXY105), Key Laboratory open project of the Ministry of Public Security (No.KF201309) and the Ministry of Public Security Fire Department project (No. 2012XFCX10).

REFERENCES

1. W.-H. Chen, W.F. Du, X.-N. Xu, X.-C. Cui and J. Ma, *Fire Safety Sci.*, **17**, 15 (2008).
2. W.-H. Chen and W.F. Du, *Fire Safety Sci.*, **17**, 330 (2008).
3. L.R. Yu, C.H. Lu, S.J. Gao, S.L. Zhao and Z.Z. Xu, *Mater. Rev.*, **20**, 52 (2006).
4. J.-X. Xiao, Z. Gao, M.-H. Wang and R.-H. Cui, *Chem. Res. Appl.*, **20**, 569 (2008).
5. Public Security's Political Department Editing, Fire Fighting Tactics, The Masses Press, Beijing (2004).
6. M.S. Vilessova, L. Ye Gendlin, L.A. Rubinchik, A.A. Bespalov and B.I. Tkachev, *Oil Hydrocarbon Spillsa*, **8**, 139 (2000).
7. A.M. Tafreshi and M. di Marzo, *Fire Safety J.*, **33**, 295 (1999).
8. Fu Bao Zhou and Wangxing Ren, *Int. J. Coal Geol.*, 95 (2006).