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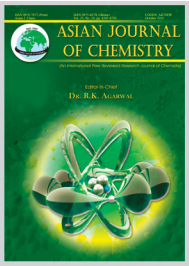

NOTE

Preparation of Spherical Powders by Hydrolyzing Solvent

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Combining the theory of esters hydrolyzing and emulsion solvent extraction method, a new method of making spherical powders by hydrolyzing solvent is developed, aiming at solving the deficiency of traditional preparation process of spherical powders (emulsion solvent evaporation technique). The powders showed a rough spherical surface and narrow size distributions under the condition: the vol./wt. ratios of solvent to NC being 3.5 mL: 1 g, uniform temperature 72 ºC, the volume ratios of 98 % H_2SO_4 to water being 1:200. The mechanism of hydrolysis reaction was validated by detection of ethanol in the distillation by gas chromatography. Comparing with the traditional process, hydrolyzing technique can shorten the reaction time and decrease the temperature, in addition, it uses constant temperature and the technological process is simplified, which would effectively prevent the softened grains aggregating.

Key Words: Spherical powders, Hydrolysis, Ethyl acetate, Preparation method.

Spherical powders are round-shapes energetic material with particle size ranging from several micrometers to several millimeters and they are especially used for small arms, such as pistols, revolvers, rifles and shotguns[1]. A process for making spherical powders is disclosed in U.S. Patent 2027114 granted Olsen, January 7, 1936[2] and it has been used to this day: the base is agitated with a solvent distributed in the non-solvent vehicle so as to form an emulsion with the medium as the internal phase; upon the addition of protective colloid the emulsion is broken and under agitation reformed, inverted with the medium as the external phase. These globules are then subjected to treatment to extract the solvent, as by distillation of the solvent secured by heating the medium to near the vapourizing of the solvent, or beyond. The process can control the character, uniformity and the process is very safe[3,4]. However, the processes are generally stereotype, tedious and it need high bathing temperature. Thus, a need exists for an improved method for producing spherical powders.

Solvent removing or organic phase separation methods[5-8] are popular techniques for the preparation of powders. Generally, there are two main ways available to removing volatile solvent in water: one is evaporation, which is used by Olsen. It is usually achieved through slow volatilization or boiling. Li *et al.*[9] synthesized ABS/PC alloy hollow micro-spheres by using W/O/W multiple emulsion solvent evaporation technique. Li *et al.*,[10] produced the IVM-PLAG-MS by a modified S/O/W emulsion solvent evaporation method. But there are some defects in this process, the solvent employed should be substantially insoluble in water and has a low boiling point than water, the boiling point of the solvent greatly influence temperature in the process, we must change the heating rate from the beginning to end of the vapourization to avoid the formation of soften particle agglomeration. Heiskanen *et al.*[11] prepared MAO micro-spheres using a solvent extraction process. However, this process needs a lot of extracting agent, which would lead to environmental pollution and it has a low yield. To overcome these shortcomings, a new process for removing-solvent forming is used to prepare spherical powders in this study *i.e.*, hydrolyzing solvent technique. In the presence of a catalyst organic solvent hydrolysis to water-soluble substances which will melts in medium (water) and it separates from the base which will take shape.

D-Nitrocellulose was purchased from Luzhou Chemical Plant (Luzhou, Sichuan Province, China); ethyl acetate, sulphuric acid, potassium bicarbonate, potassium nitrate and gelatin were purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). All drugs were of analytical grade. Water bath kettle and agitator were made by 311-teaching and research section of Nanjing University of Science and Technology; a SP-1000 gas chromatograph (Beijing Beifeng Instrument Factory, China) was used to analyze the product of hydrolysis.

Putting 350 mL ethyl acetate and 100 g D-nitrocellulose into a 3-mouth flask, stirred, heated at 72 ºC in water bath for

TABLE-1
CONTRAST OF THE TWO PROCESS OF THE PRODUCTION OF SPHERICAL POWDERS

	Process	Dissolution	Emulsifying	Pre-evaporation	Dehydration	Evaporation
Removing solvent by evaporation	Reaction temperature (ºC)	66-69	66-69	70-73	66-69	69-72, 72-74, 74-97
	Reaction time (min)	60-90	60-120	60-150	60-120	90-120, 60-90, 90-120
	Process	Dissolution	Emulsifying	Dehydration	Hydration	Neutralization
Removing solvent by hydration	Reaction temperature (ºC)	72	72	66-69	72	72
	Reaction time (min)	30-60	30-60	60-120	60-120	5-10

1 h. A total of 800 mL water is then added into the flask and then gelatin. After the small drops of lacquer becoming spherical, add 800 mL 8.9 % sodium sulfate solution to the flask and dehydrating for 3 h and then adding 100 mL of 0.9 mol/L sulfuric acid solution. When the softened grains become hardened while retaining their globular shape, the compound is added by potassium bicarbonate to neutralizing the said acid. Separate the powders and soak it in water, then dry the powders for use.

The product of hydrolysis were vapourized and dried and, then were analyzed by GC equipped with a flame ionization detector (FID) and a capillary column. The temperatures of the detector and the oven were 150 ºC and 200 ºC, respectively. Nitrogen was the cattier gas at a flow rate of 40 mL/min.

Mechanism of the process: The mechanism of the process may be as follow: oil-soluble ethyl acetate hydrolysis to water-soluble acetic acid and ethanol under acid condition, which will transfer from the dispersed phase (NC droplets) to the continuous (water). When most of the solvent transfer by dispersing the organic phase into the aqueous phase, the NC base becomes harden powders. If we prove acetic acid or ethanol in the reaction system the hydrolysis reaction of ethyl acetate can be right. For simplicity, ethanol was detected by gas chromatography. There are inorganic salt and acid, which would interference testing in the aqueous phase, distillation and drying steps is adopted. We collected two samples for comparative analysis, sample 1 is the distillation before adding inorganic acid, sample 2 is the distillation after the powders take shape.

Using ethanol and ethyl acetate as the standard material, the retention time was 15 min and 21 min, respectively. Single peak was detected in sample 1 and the retention time was 21 min, which demonstrated no ethanol in reaction system before acid was added. Two peaks were detected in sample 2 and the retention time was 15 min and 21 min, which demonstrated ethanol and ethyl acetate were existed in reaction system. The result showed ethanol was produced in the experiment, which proved that the mechanism of hydrolysis was correct.

Contrast of the new and traditional process: The powders made by hydrolyzing showed a rough spherical surface and narrow size distributions and the effect of molding by hydrolyzing and vapourizing are on the same level. The process of traditional distillation is preferably carried out by effecting vapourization at a rate decreasing from the beginning to the end of the vapourization period and at a rate less than the rate of diffusion of the solvent from the interiors to the exteriors of the globules. Such a distillation secures a solid grain as distinguished from one which is porous. This process need a long time to vapourizing the solvent employed and also high bashing temperature, which often leads to the softened grains agglomerating and results in the failure of the experiment. In additional, the traditional distillation needs high bathing temperature. In short, there are many disadvantages in the traditional distillation. However, the new process of hydrolyzing the solvent employed for manufacture of spherical powders saves time, uses maintaining 72 ºC, which is greatly lower than the traditional temperature and further provides for a more practicable and effective way of removing solvent. The organic solvent can also be recovered in the new process if necessary. The two process of making spherical powders are shown in Table-1.

Conclusion

Combining the theory of esters hydrolyzing and emulsion solvent extraction method, a new method of making spherical powders by hydrolyzing solvent is developed, aiming at solving the deficiency of traditional preparation process of spherical powders (emulsion solvent evaporation technique). The powders showed a rough spherical surface and narrow size distributions and the effect of molding by hydrolyzing and vapourizing are on the same level.

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