WAX MICRONISATION

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Rapid Expansion of a Supercritical Solution (RESS) was used to micronise commercial synthetic waxes, with congealing points ranging between 80 and 110 ºC. Propane was used as supercritical solvent, because of its high solvent power for paraffins. Porous plate nozzles, with pore sizes of 15, 25 and 60 µm were used. Number average particle diameters ranged between 1.0 and 1.5 µm. The most favourable conditions for the formation of small, spherical wax particles was found to be at the lower pre-expansion temperatures (130-160 ºC) and higher pre-expansion pressure (150-175 bar). Higher wax concentrations seems to give rise to smaller particles, but at concentrations in excess of 5 wt %, coagulation of smaller particles seem to cause an increase in particle size and formation of irregularly shaped particles. The higher melting point wax gave particles of more spherical shape than the lower melting point wax. It is speculated that the higher percentage of oil in the lower melting point wax stays in solution for a longer period of time, and precipitates on the surface of already formed particles where it serves as a "glue" that holds smaller particles together.

INTRODUCTION

Synthetic wax consists of a mixture of straight and branched alkanes. When added to powder and solvent based coatings, synthetic wax will improve, amongst others, the abrasion resistance, water repellence and slip of the coating. The texture and gloss of the coating is influenced by the size and shape of the wax powder particles in these coatings. Spherical wax particles, with a diameter of 5 µm or less, will give the coating a glossy appearance and smooth texture.

Current techniques of wax micronisation include spray solidification and grinding processes such as jet milling. Non-spherical wax particles, larger than 20 µm in diameter, are obtained from jet milling. Spray solidification yield the desired product, but a significant percentage of the particles are outside the desired size range, resulting in costly classification and wax recycling.

The use of supercritical fluids as a means to fractionate and separate synthetic wax mixtures has been studied [1,2]. It was found that supercritical fluid processing could be a viable option to replace existing technologies in these fields. Should supercritical fluid micronisation processes be suited for wax micronisation, it would add to the viability of implementing a supercritical fluid wax processing unit.

Rapid Expansion of Supercritical Solutions (RESS) is a crystallisation process whereby the solvent power of a supercritical solvent is rapidly decreased by expansion over a nozzle, resulting in high supersaturation and very low crystal growth periods. It has been used in studies to produce powders of pharmaceuticals [3,4], polymers [5,6], and inorganic compounds [7]. High pressures and low solute concentrations count against the RESS process. Paraffin wax micronisation with supercritical fluids has been attempted before [8, 9]. In these wax micronization RESS studies high pressure (>170 bar), high temperature (>170 ºC) and low concentrations (< 0.2 mass %) were needed to yield particles of suitably small

size. Despite this, RESS is a more attractive option than anti-solvent processes (GAS, SEDS, ASES) where removal of solvent residue from the product can be problematic.

In this study propane was chosen as supercritical solvent since lower pressures are required to solubilise a given mass fraction of paraffin wax compared to ethane or carbon dioxide, which is generally the solvent of choice [10,11].

Traditionally, capillary nozzles have been the popular choice, but porous plate nozzles have been suggested as expansion device. Using the same conditions, it was proven that the porous plate nozzles could yield smaller particles than capillary nozzles [3]. Porous plate nozzles consist of a network of metal and pores, resulting in higher mass flow rates and lower pressure drop due to streamline contraction of the entering solution. Its particular geometry makes it less likely to block and cheap to replace and is thus an attractive option for use on industrial scale.

The aim of this study was to investigate the effects of pre-expansion temperature and pressure, concentration and nozzle morphology on the particle size, shape and distribution of two synthetic waxes.

EXPERIMENTAL

The experimental apparatus that was used in this study is shown in Figure 1.

The wax was weighed and loaded into a cell (C, 45 cm^3). The cell volume was evacuated (~80 Pa), after which propane was added from a cylinder via the soft seat valve (F). Dowtherm heating oil, maintained at a preset temperature in an oil bath (E), is passed through the jacket around the cell to control the temperature. Regulated electrical heating tape (Thermon TSX) was tightly connected to the line (¼" SS tubing), the soft seat valve and the spraying nozzle to provide additional heating.

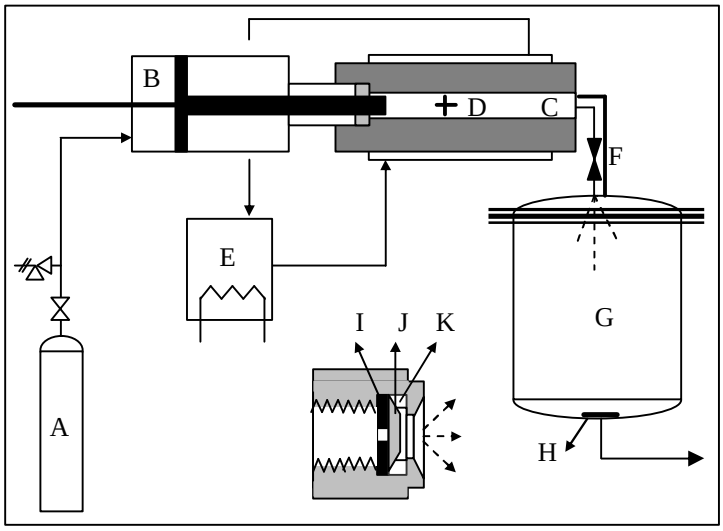

Figure 1: Experimental Set-up for RESS

A counterbalance piston (B, 13:1 area ratio), was used to pressurise the cell content. Nitrogen (A), regulated up to 17 bar, was used to apply pressure to the larger area of the piston. The pressure in the cell was measured with a melt pressure sensor (±0.1 bar).

The cell content was agitated for 3 hours with a magnetic stirring cross (D) to ensure good phase equilibrium prior to expansion. After the equilibrium period, the cell content was expanded over the nozzle by rapidly opening the shut-off valve (F), allowing the solution to flow through the nozzle into an enclosed expansion chamber (G). The porous plate nozzles were attached directly onto the valve (F). A standard ¼" stainless steel nut housed the porous plate. Double seals are provided, with an aluminium washer (I) between the valve and porous plate (J) and a teflon ring (K) at the front between the nut and porous plate. The porous plate cross sectional area exposed to the entering solution was circular, with a diameter of 3 mm.

The cylindrical expansion chamber were of large enough diameter (± 1 m; length 1 m) to prevent the spray cone from hitting the sides. As soon as the cell volume reached a minimum (~8 cm^3), the valve was closed. Vacuum was applied across a paper filter (H)

attached at the chamber outlet, to draw the propane from the chamber, causing wax particles to be collected on the filter paper.

The wax filter cakes were quartered, thoroughly mixed and dispersed on an SEM stub by addition of a few drops of methanol. Samples were pulse sputtered with gold to improve the quality of SEM photographs. The analyses were done by taking SEM images on a LEO S440 and measuring particle sizes with the analysis package Scionimage.

The propane used was obtained from BOC Gases with purity of better than 97 %. Butane was the main impurity. Commercial Paraflint C80 (cong pt: 82 ºC, oil content 0.75 wt%) and Paraflint C105 (cong pt: 108 ºC, oil content <0.1 wt%) waxes were used in the micronisation experiments.

RESULTS AND DISCUSSION

Phase Behaviour of Wax and Propane Mixtures

An thorough understanding of the phase behaviour of the supercritical solvent + solute system is imperative in determining where one- or two-phase conditions will exist. A typical propane + alkane phase diagram is shown in figure 2. It is important to note that complete miscibility can be obtained at relatively low pressures. More detail on the phase equilibria of ethane and propane with high molecular weight alkanes can be found in the work of du Rand [10] and Schwarz [11].

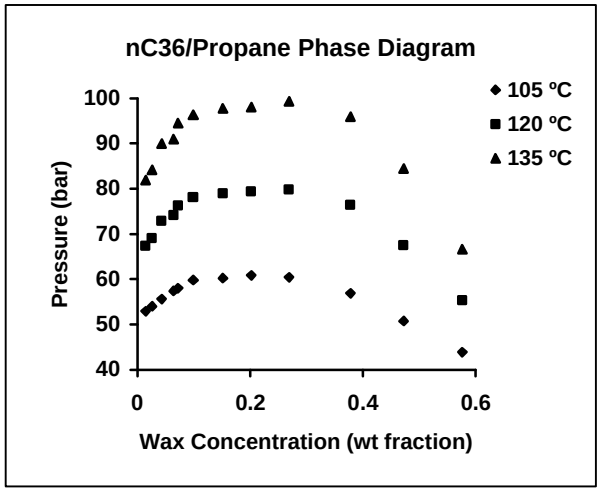

Figure 2: Wax/Propane phase behaviour [11]

Experimental Runs

Solutions of C80 and C105 wax (1-6 wt%) in propane were expanded through porous plate nozzles of diameters 15, 25 and 60 µm. Pre-expansion temperatures of 130 and 160 ºC and pre-expansion pressures of 150 and 175 bar were investigated.

Particle Size and Distribution

For the whole range of experimental parameters investigated, a number average particle size of between 1.0 to 1.5 µm was found, which was well within the target value of 5.0 µm. A lognormal size distribution was observed in all cases. The influence of the parameters on particle size was not as significant as the influence it had on particle shape.

Influence of Wax Type

It was found that the C105 wax yielded more discreet and spherical particles than the C80 wax. Since the C80 wax contains more oil than the C105 wax, it could be that this oily components, being more soluble in propane, precipitates on the C80 particle surface after the particle has formed. This could result in softening of the wax surface and in the same time serve as a type of glue that causes colliding particles to deform and stick together. In Figure 3 an example of the difference in the particle shape of the the C80 and C105 wax particles is shown.

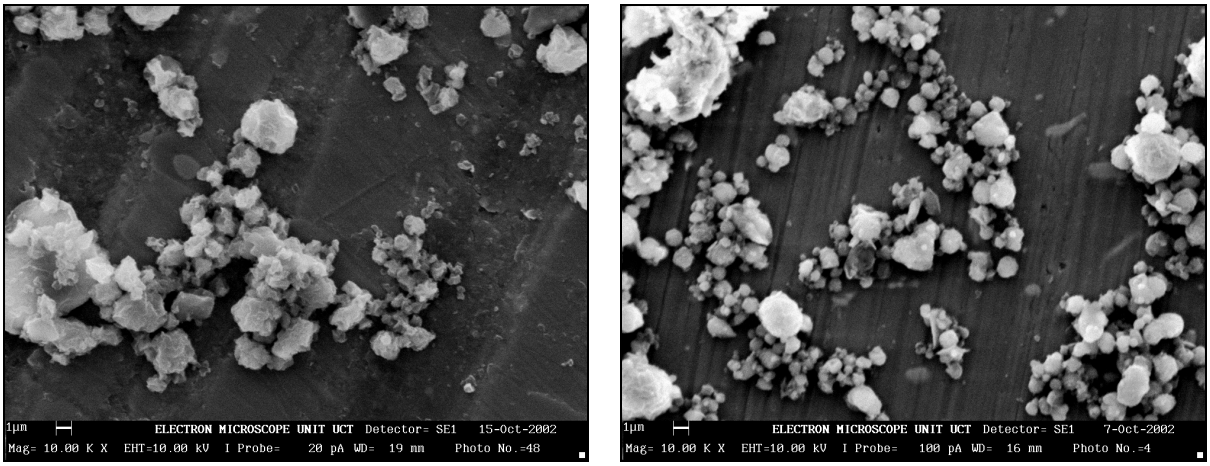

Figure 3: Comparison of C80 (left) and C105 (right) wax particles obtained from a wax concentration of 2 wt %. Pre-expansion pressure and temperature: 175 bar, 130 ºC. Nozzle: 60 µm average pore diameter.

Influence of Temperature and Pressure

It was found that a pre-expansion temperature and pressure combination of 130 ºC and 175 bar yielded particles that are more spherical in shape compared to those formed at other conditions. This is clearly visible in Figure 4, where the difference in the particle shape is quite marked. The more favourable conditions correspond to conditions furthest away from the dew point of the solution. It is thus believed that the onset of particle formation is further downstream in the nozzle for this combination, resulting in a smaller particle growth period. If the particle formation is delayed until very close to the nozzle outlet, or even the free-jet, the less severe particle deformation due to coagulation and agglomeration effects will be.

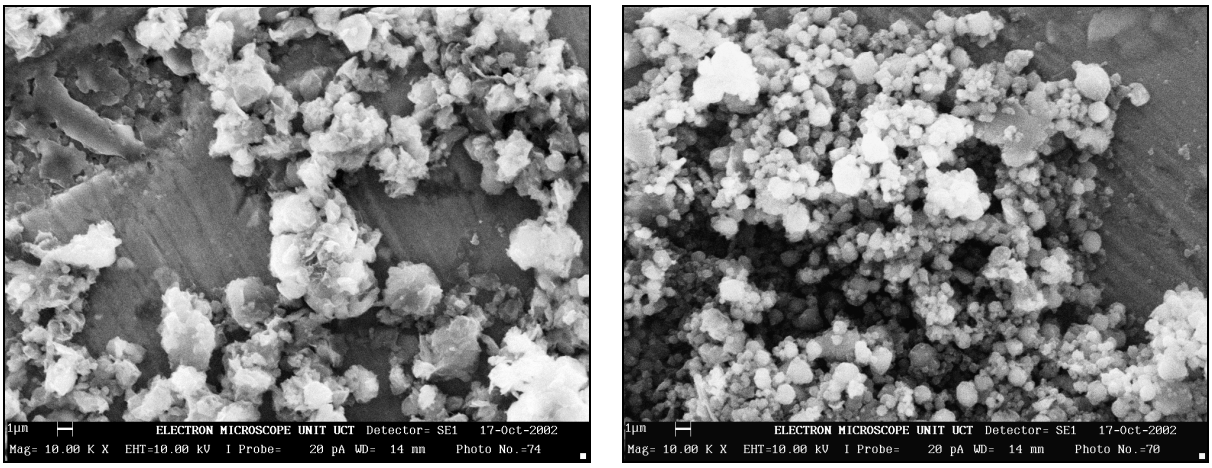

Figure 3: C105 wax particles obtained from pre-expansion conditions of 150 bar, 160 ºC (left) and 175 bar, 130 ºC (right). Nozzle: 60 µm average pore diameter. Wax concentration: 5 wt %

Influence of Wax Concentration

Concentration had quite a marked effect on the particle shape. This is evident from figure 5, where the particle shape changed from reasonably spherical to irregularly shaped particles as the wax concentration is increased beyond approximately 5 mass%. From particle