High Output Coating R&D,

Accelerating the Process from Discovery to Commercial Output

Josef Schroer[*]

[*]Chemspeed Technologies, 7 Deer Park Drive, Suite L
Monmouth Junction, NJ 08852, josef.schroer@chemspeed.com

ABSTRACT

The use of automated High Output Technologies has expanded from its origins in Biotech and CombiChem into laboratories of many other areas in the chemical industry. New fields like Polymer- and Material Sciences, which strongly affect the Pigment and Coating industry, successfully have implemented High Output Technologies to significantly increase their productivity.

For this reason instruments similar to the equipment, which originally has been designed to accelerate the process of Drug Discovery, now commonly also is being is found in Polymer and Material Sciences laboratories where multiple dispensing and mixing of liquids, solids and gases under controlled conditions represents one of the core requirements.

Additional requirements to these instruments strongly depend on the particular workflow and are governed by the characteristics of the individual application. Those needs might cover a very broad and complex range of unit operations.

For this reason only flexible, highly modular, and scalable equipment has the chance of covering the diverse R&D needs of these industries.

The general requirement for increased output & efficiency has boosted the continued evolution of automated laboratory equipment.

Using selected examples, from the Pigment and Coating Industry, this presentation will show how a variety of challenging parallel workflows fully have been automated.

1 HISTORY OF HIGH OUTPUT EXPERIMENTATION

The field of high-output experimentation recently has emerged as a promising technology to accelerate research in biotechnology, pharmaceutical industry as well as in the chemical industry and materials science. Contrary to its view as modern topic, the first examples date back more then a hundred years; the first scientist to apply parallel methods was *Thomas A. Edison* [1,2]. In his efforts to find a suitable filament for electric bulbs, he tested more then 1600 different materials before finding carbonized cotton threads as the material of choice. His scientific work is written down in more than 3000 notebooks with 280 pages each and provided results for almost 2500 granted patents.

In 1912 the Italian chemist *Giacomo Ciamician* placed hundreds of reaction flasks on the roof of the university of Bologna in search of a photoactive substance for a photochemical process [3] (Figure 1).
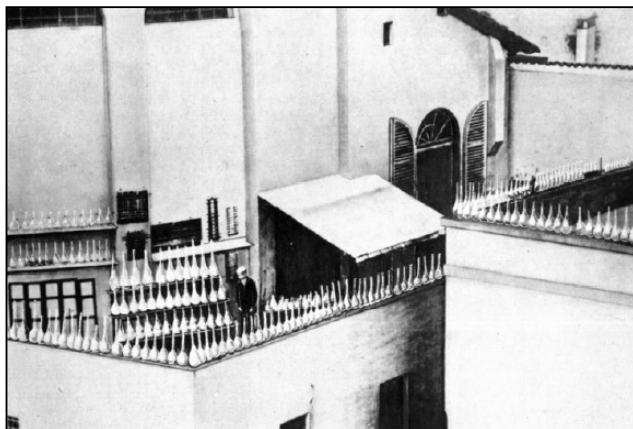

Figure 1:
Parallel set-up for photochemical processes in the early years of the 20th century placed on the roof of the University of Bologna by Professor Giacomo Ciamician.

A contemporary catalogue supplying chemical laboratory equipment among parallel extractors and shakers even offered an autoclave suitable for twelve parallel pressurized reactions with up to 10bar (Figure 2) [4].
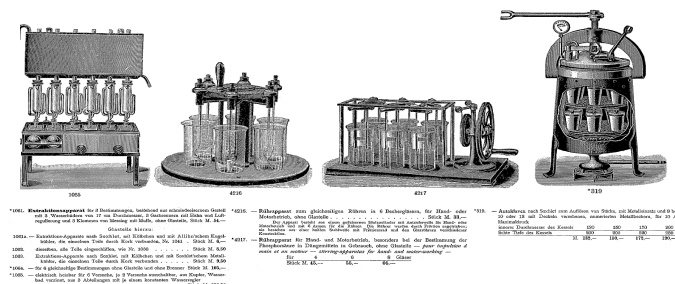

Figure 2:
Contemporary examples of chemical laboratory equipment including parallel extractors, stirrers and pressurized reactors.

Almost one hundred years later the very same principle is still applied in state-of-the-art equipment for parallel reaction screening under elevated pressure (Figure 3, Symyx HiP reactor and Chemspeed parallel pressure reactors [5].
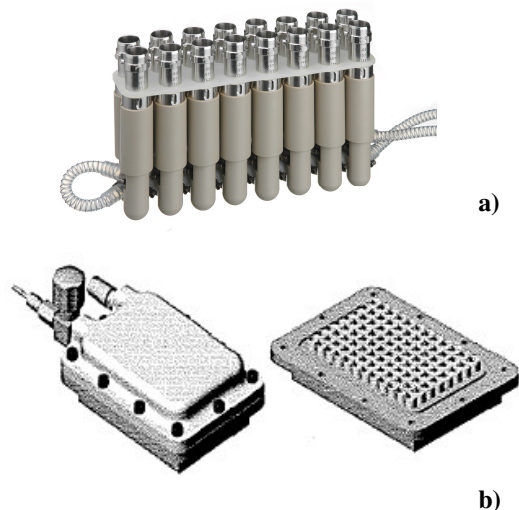

a)

b)

Figure 3;
State-of-the-art equipment for parallel reactions under elevated pressure: a) Symyx's HiP-reactors and b) Chemspeed's array of 16 parallel pressure reactors.

Although representing an impressive commitment, the early approaches towards parallel and combinatorial experimentation naturally were lacking any automation, so that the analysis of the results was an extremely time consuming task. Consequently, these new ideas were not taken up by other chemists, since they generated new bottlenecks.

After first initiatory works in the 1960s [6,7], *Joseph J. Hanak* is now recognized as the pioneer of the modern high-output experimentation. He was the first author to report on the automated preparation and analysis/screening of libraries of inorganic materials in search of new superconductors [8,9].

Nevertheless, this new methodology did not become not popular among the scientific community because of the general lack of computers at that time, which were essential for automated testing and data processing [10]. This changed at the end of the 1980s, when impressive progress in laboratory automation equipment was achieved trough the common availability of computers.

Today, every step of a specific workflow starting from solid & liquid handling, reaction & formulation control, purification, analysis and finally screening can be automated with suitable robotic equipment. In the following sections applications of such automation equipment in synthesis and formulation of materials essential for the coating industry are described.

2 PREPARATION OF STABLE NANOLATEX SUSPENSIONS ON THE CHEMSPEED MINIPLANT TECHNOLOGY [11]

Latexes find widespread use in coatings, textiles and adhesives industries. Functional groups can easily be incorporated into the polymer particles and/or the polymer particle surface. Nanolatexes are characterized by a smaller particle size (diameter usually smaller than 30 nm), resulting in a significantly higher specific surface area (up to 400 m^2 g^{-1} for particles with diameters ~15 nm) and thus a higher functionality which increases the number of applications of the products.

Microemulsions are thermodynamically stable dispersions of droplets less than 30-40 nm in diameter. They are formed spontaneously from mixtures of water and monomer containing large amounts of surfactant. In the process described below, the amount of surfactant is far lower and the polymer concentration is significantly higher, compared to typical microemulsion polymerization processes, giving a higher ratio of polymer/surfactant in this system.

The methodology for the synthesis of a stable nanolatex suspension is outlined in Figure 4: An aqueous solution containing a surfactant and an initiator is heated and monomer solutions added via two separate feed-pumps. Once the monomer conversion is near quantitative (>99%), the reaction is quenched, residual free monomer is removed and the final sample is characterized.
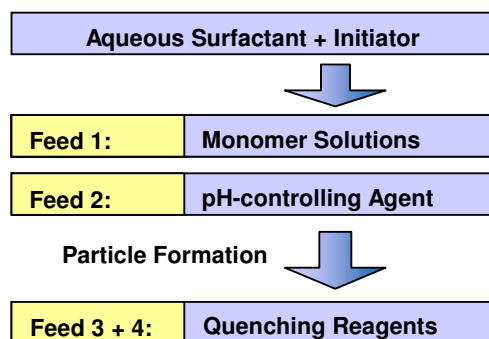

Figure 4:
Schematic work flow for nanolatex preparation

A stable nanolatex was easily obtained using Chemspeed's MiniPlant technology. Stirring speed was shown to have a major influence on the size of the formed particles, as shown in Figure 5. High stirring speeds and thus high sheer force leads to increased particle size. Different types of stirrers could also be tested such as triple helix and anchor designs.

The calorimetric profile of the reaction is shown in Figure 5, clearly showing that the reaction does not emit significant heat (is not exothermic). The increase in the jacket temperature (red) over time is due to an increasing reaction volume, caused from the various feeds.
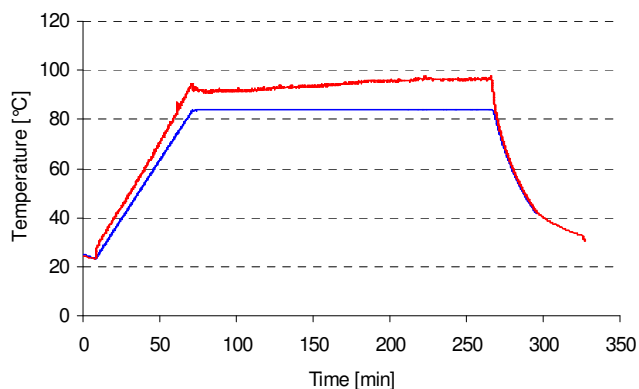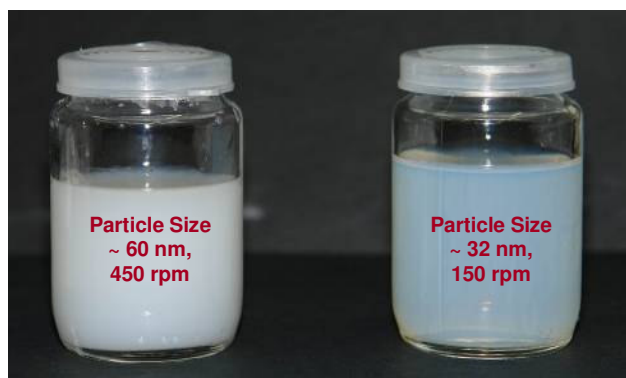

Figure 5:
Up: Schematic workflow for nanolatex preparation Effect of stirring speed on the particle size at 450 rpm and at 150 rpm.
Down: Calorimetric data obtained from the reaction; jacket temperature (red), reaction temperature (blue)

3   EMULSION POLYMERIZATION ON THE CHEMSPEED MINIPLANT TECHNOLOGY [12]

Free-radical emulsion polymerization is a process that involves the emulsification of monomers in a continuous aqueous phase, and stabilization of the initial droplets and final latex particles by a surfactant such as sodium dodecylsulfate (SDS). Surfactants have a large influence on the latex product properties, e.g. particle size distribution, molecular weight and rheological properties. Stirred tank reactors are commonly employed for the synthesis of such latexes.

Optimization of emulsion polymerization conditions is often a very time-consuming process, making them a perfect candidate for the application of high-throughput experimentation. To demonstrate this point, the well-known system of styrene-polymerization was chosen for this study.

Emulsion polymerization is often started via well-defined degradation of a peroxide and excellent control is crucial in order to obtain reliable and reproducable results. The polymerization sequence with sodium persulfate as radical initiator is shown in Figure 6.
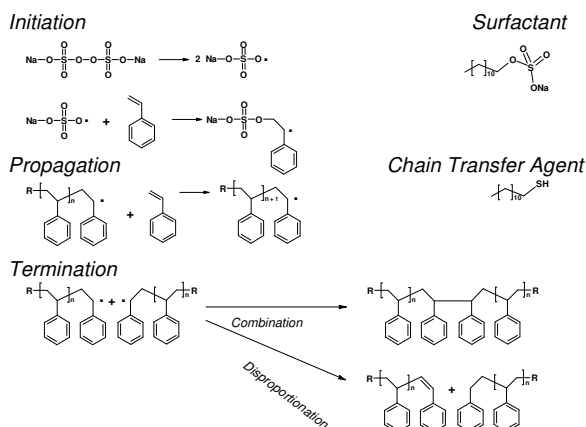

Figure 6:
Reaction mechanism for the radical-induced styrene-polymerization

The emulusion polymerization of styrene is occurring in different intervals:

- *Interval I:* Water insoluble monomer in aqueous solution containing a surfactant resulting in large monomer droplets and micelles with small amounts of monomer.
- *Interval II:* Primary free radicals from the initiator react with monomer in aqueous phase to produce oligomeric radical species that subsequently diffuse into monomer-swollen micelles.
- *Interval III:* Propagation within micelles is supported by diffusion of monomer from the aqueous phase. Micelles grow and incorporate other surfactants from micelles which were not initiated.
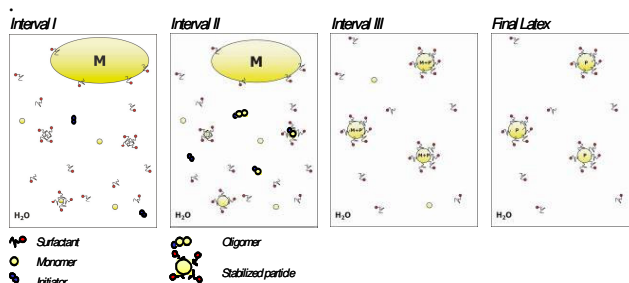- *Final Latex:* Whole monomer is consumed and termination occurs within the micelles.

Figure 7:
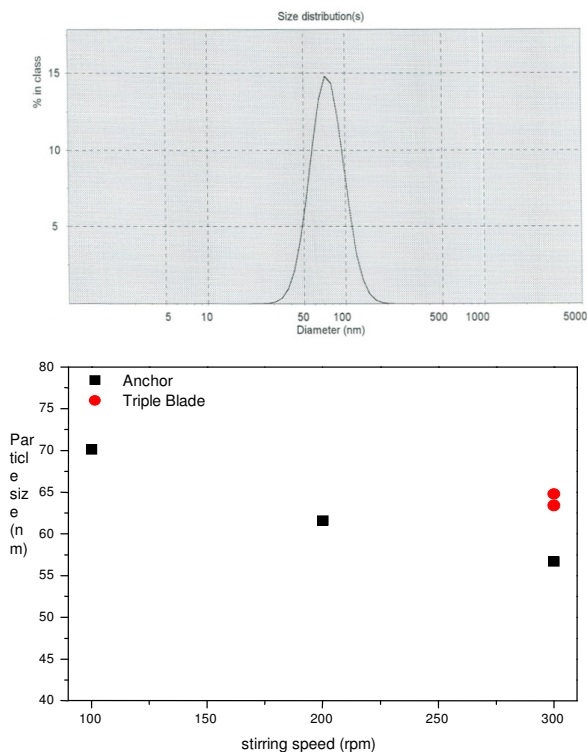Intervalls in the Emulsion Polymerization of Styrene

Figure 8:

Up: Particle size distribution measured by dynamic light scattering (DLS) techniques from a polystyrene emulsion polymerization (20 wt-%) with an anchor stirrer.

Down: Effect of stirring speed on the particle size for the anchor and triple blade stirrers.
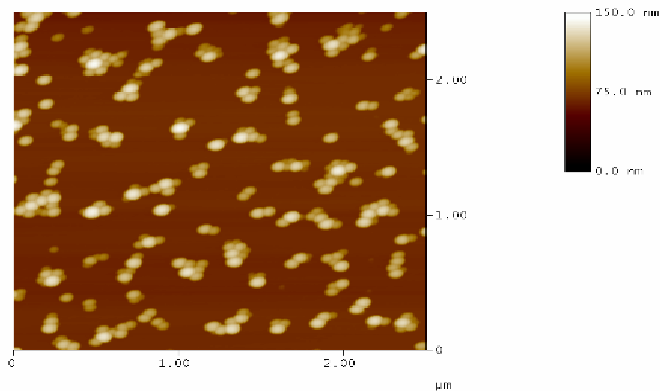

Figure 9:

Atomic force microscopy (AFM) images of polystyrene particles from an emulsion polymerization performed on the AutoPlant (20 wt-%) equipped with an anchor stirrer

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