# Latex Optimization for Emulsion Aggregation Toners with Design for Lean Six Sigma (DfLSS) Methodology

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## Abstract

*Design for Lean Six Sigma (DfLSS) is a systematic methodology to design new products or processes so that quality is built into every phase of product design. It is also a proven process improvement methodology used for improving existing products through redesign, and currently widely being employed across chemical industry. This paper describes the application of DfLSS methodology for the formulation and process design of an improved emulsion latex for emulsion-aggregation toner application. A systematic IDOV process (Identification, Design, Optimization and Validation) was demonstrated from the point of view of the research scientist/engineer. The key customer requirements were "designed-in" via the latex key properties (Tg, Mw and particle size) and optimized through DOEs (design of experiment). The resulting latex process is more robust against several sources of variation (raw material quality, operation and equipment aging). This was accomplished through a robust design and implemented at the manufacturing scale.*

## Introduction

Design for Lean Six Sigma (DfLSS) is a systematic methodology using tools, training, and measurements to enable the design of products, services, and processes that meet customer expectations at Six Sigma quality levels. Typically, Design for Six Sigma follows IDOV four-phase process that consists of Identify, Design, Optimize and Verify, as shown in Figure1. Different tools can be used at each phases [1] .

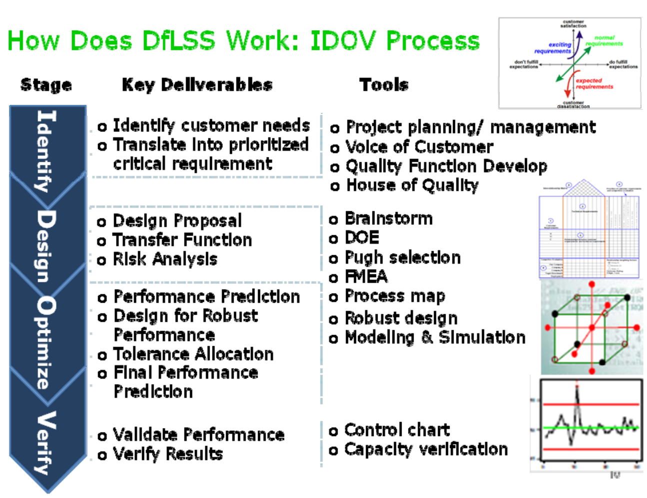



***Figure 1**. Design for lean six sigma (DfLSS) IDOV process.*

The Identify phase begins the process with a formal tie of design to Voice of the Customer. This phase involves developing a team and team charter, gathering VOC, performing competitive analysis, and developing CTQs. The Design phase emphasizes CTQs and consists of identifying functional requirements, developing alternative concepts, evaluating alternatives and selecting a best-fit concept, deploying CTQs and predicting sigma capability. The Optimize phase requires use of process capability information and a statistical approach to tolerancing. Developing detailed design elements, predicting performance, and optimizing design, take place within this phase. The Validate phase consists of testing and validating the design. As increased testing using formal tools occurs, feedback of requirements should be shared with manufacturing and sourcing, and future manufacturing and design improvements should be noted. Figure 2 summarized the comparison between Six Sigma and Design for Six Sigma [1].

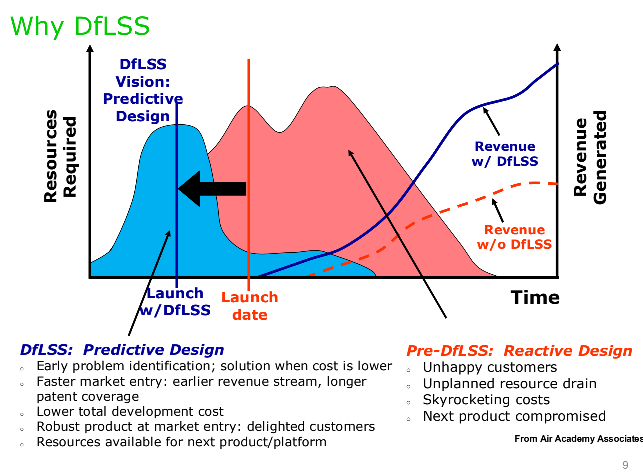



***Figure 2**. Why Design for lean six sigma (DfLSS).*

Chemically produced toners (CPT) have attracted more and more attention both in academic studies and industrial application for digital printing. Depending on the chemical process used for the preparation of toner, CPT can be made through suspension or dispersion polymerization, emulsion aggregation, and chemically milling process [2-4]. Compared with conventional toner process (mechanical grinding process), CPT approaches to toner offers advantages such as smaller toner particle size and narrower size distribution, higher toner transfer efficiency in the machine and better image quality [5]. Among all the CPT processes, emulsion aggregation (EA) process offers more tunability on particle design, especially on particle composition, structure, and morphology and shape factor. EA process consists of aggregating polymeric particles prepared by emulsion polymerization (latex) with pigment and other toner components. Typically, in EA process, the toner particles are produced directly from submicron polymer particles dispersions, by mixing latex prepared by emulsion polymerization with pigments and other ingredients (also dispersed in aqueous phase)[5, 6]. All the latex and pigments dispersion are negatively charged. Then a flocculated agent was added into the mixture (typically positively charged) and aggregate particles ranged from 0.8 to 2 micron can be formed through the aggregation of latex and pigment particles. This is referred as primary aggregation. The primary aggregates can the further grow to the 5 to 10 micron in diameter through secondary aggregation under carefully controlled operating conditions. Finally, those aggregates went through a coalescence step under which the particles are fused into homogeneous toner particles of controlled shape by heating above the glass transition temperature. Toner particle shape and size distribution are important factors in determining the electrophotographic printing machines performance and the final print image quality, especially for advanced high-resolution and color printings.

The latex quality (particle size, size distribution, molecular weight and weight distribution) is very important for EA toner [7, 8]. A robust latex making process is often critical to produce high quality of latexes with very tight specification as required by EA toner process.

## Experimental

**Semi-Continuous Emulsion Polymerization:** In a 300L jacketed stainless steel reactor, a certain amount of anionic surfactant, and deionized water were charged in, and deaerated for 30 minutes while the temperature was raised to 75°C. A monomer emulsion was prepared by agitating a monomer mixture of certain amount of styrene, n-butyl acrylate, the functional monomer acryloxypropionic acid with an aqueous solution (certain amount of anionic surfactant and deionized water) at room temperature. All the chemicals were from Sigma-Aldrich. 1 wt% of the pre-made emulsion was taken as the seed emulsion and added into the reactor and was stirred for 10 minutes at 75°C. An initiator solution prepared from certain amount of ammonium persulfate in deionized water was fed into the reactor over 20 min. Stirring continued for an additional 20 minutes to allow seed particle formation. The remaining monomer emulsion was fed into the reactor at a control rate over 4 hours. At the conclusion of the monomer feed, the emulsion was post-heated at 75°C for 3 hours and then cooled. The final latexes were characterized for particle size (MicroTrac).

**EA toner particle preparation:** All the toner particles in this paper were prepared in a 2L glass reactor using the following process. In a 2L beaker, 258 grams styrene-butyl acrylate latex (particle size of 220 nm), 80.0 grams pigment dispersion (magenta, or black), and de-ionized water 670 grams were mixed by a homogenizer for 15 minutes at 20 ºC. Then a flocculate agent was added dropwise in 5 minutes. The resulted viscous mixture was continuously mixed by a homogenizer for another 20 minutes to form primary aggregates with particle size of about 2.0 micron. Then the homogenizer was removed and the mixture was transfer into a 2L glass reactor. And the temperature of the mixture was raised to 50ºC in about 35 minutes under a mechanical stirrer mixing at 550 rpm. After the particles reach at 5.8 micron, 140 grams shell latexes (the same as the core latex) were added dropwise in 10 minutes. After particle size reached at 6.5 microns, a freeze agent was added to stop the particle growth and hold for another 20 minutes. Then, the temperature of the mixture was raised to 90 to 96 ºC in 35 minutes and hold for certain time. The mixture was cooled down to 35. After washing de-ionized water, acid and DI-water, and dried at 45ºC, the final toner product has a volume median particle size of 6.0 microns.

## Robust Design for EA Latex

IDOV process in EA latex robust design: A systematic IDOV process (Identification, Design, Optimization and Validation) was followed. Figure 3 outlines the Identify Stage deliverables. After this stage, the key customer requirements were identified through voice of customer (VOC).

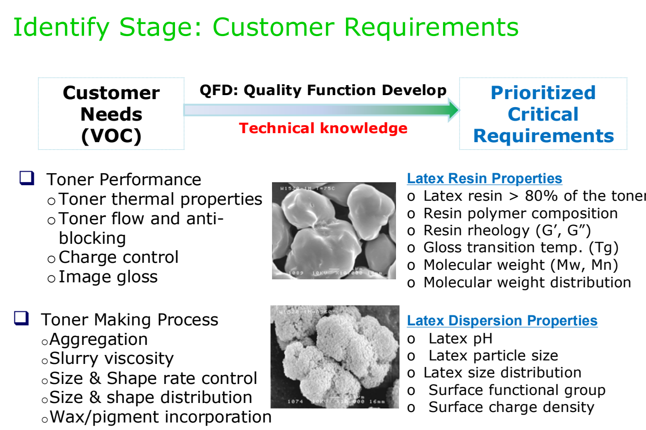
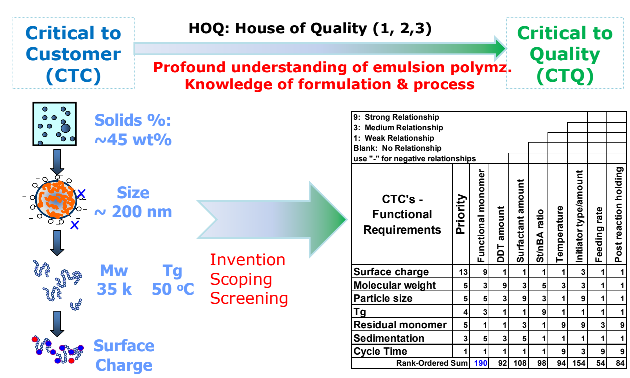



*Figure 3. Identify Stage: Customer Requirments*

The identified Critical to Customer (CTC) requirements were transferred into Critical to Quality design parameters through House of Quality exercise. An example is shown in Figure 4.




| CTC's - Functional Requirements | Priority | Functional monomer | DDT amount | Surfactant amount | St/nBA ratio | Temperature | Initiator type/amount | Feeding rate | Post reaction holding |
|---|---|---|---|---|---|---|---|---|---|
| Surface charge | 13 | 9 | 1 | 1 | 1 | 1 | 3 | 1 | 1 |
| Molecular weight | 5 | 3 | 9 | 3 | 5 | 3 | 3 | 1 | 1 |
| Particle size | 5 | 5 | 3 | 9 | 3 | 1 | 9 | 1 | 1 |
| Tg | 4 | 3 | 1 | 1 | 9 | 1 | 1 | 1 | 1 |
| Residual monomer | 5 | 1 | 1 | 3 | 1 | 9 | 9 | 3 | 9 |
| Sedimentation | 3 | 5 | 3 | 5 | 1 | 1 | 1 | 1 | 1 |
| Cycle Time | 1 | 1 | 1 | 1 | 1 | 9 | 3 | 9 | 9 |
| Rank-Ordered Sum | | 190 | 92 | 108 | 98 | 94 | 154 | 54 | 84 |

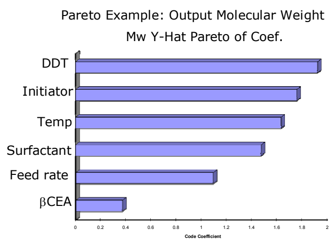
*Figure 4. CTC to CTQ*

The identified key customer requirements were then "designed-in" via the latex key properties (Tg, Mw and particle size) and followed by optimization through DOEs (design of experiment) and verification. Figure 5 shows an example of a DOE to screen the key factors on controlling the above key properties during Design Stage.

Design Stage: Formulation & Process

- Taguchi L12 DOE, to screen **8** factors
- Input: CTQ (critical formulation & process parameters)
- Output: CTC (Primary latex properties)

| Factor | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| Row # | βCEA | DDT | St-nBA | Surfactant | Temperature | Initiator | Feed rate | Holding Time |
| 1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| 2 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 |
| 3 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | -1 |
| 4 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | 1 |
| 5 | -1 | 1 | 1 | -1 | 1 | 1 | -1 | 1 |
| 6 | -1 | 1 | 1 | 1 | -1 | 1 | 1 | -1 |
| 7 | 1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 |
| 8 | 1 | -1 | 1 | -1 | 1 | 1 | 1 | -1 |
| 9 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 |
| 10 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 |
| 11 | 1 | 1 | -1 | 1 | -1 | 1 | -1 | -1 |
| 12 | 1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 |




- Follow on DOEs to define transfer functions: $\mathbf{Y} = \mathbf{f}(x_1, x_2 \dots x_n)$
- Formulation & process conditions finalized

*Figure 5. Design Stage: Screening DOE*

## Conclusions

Emulsion polymerization is a segregated free radical polymerization. Both formulation & process play critical role on final product properties. Design for Lean Six Sigma (DfLSS) is a systematic methodology to design new product or process. By using a disciplined set of tools, a specialty latex product was optimized for emulsion aggregation toner applications following IDOV process.

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## Author Biography


*Dr. Zhen (Jerry) Lai holds a Ph.D. degree in Chemical Engineering. He worked for Xerox Corporation in developing and delivering chemically produced toners for digital printing application. Dr. Lai has extensive background and experience in polymer colloids synthesis and characterization, colloidal surface and engineering. Dr. Lai is Certificated Black Belt for Design for Lean Six Sigma, who has more than 13 patents issued in chemical toners.*

*Dr. Chieh-Min Cheng is a Principal Engineer and the Manager of the Chemical Toner Delivery Area in Xerox Corporation. He has worked at Xerox for over 16 years in both the toner design/manufacturing and thermal ink jet technology areas. He holds 76 U.S. patents on graphic art imaging, ink, toner, photoreceptor, and electronic paper technology. Dr. Cheng received his M.S. in Chemical Engineering and Ph.D. in Polymer Science and Engineering from Lehigh University. He came to Xerox from a scientist position at Polaroid Corporation in 1995*