There is no doubt that statistically designed experiments can be the best approach used to optimize formulas and processes. This approach to project planning for formulation and process development is not new; it has been used for decades by scientists. The development of the software to utilize the design of experiments (DOE) approach from, initially, a main frame computer to the use with present day PC’s is critical for the experimenter. This availability of software makes this approach to experimentation very viable. Formulation development is well understood and the steps involved in the process are defined in most industries. But even today, experimenters and formulators still take the one step at a time approach to develop data. In the one step at a time approach, it is still difficult to account for the complex interactions of some ingredients in a formula or process without doing a very large number of experiments. A review of the steps involved in basic formulation approaches will be discussed. The use of DOE software to determine the number of experiments to produce formulas with optimal properties will be presented. Examples of designs as well as the results will be presented on how DOE can be effectively used.
Agenda

- Introduction
  - Formulation Principles
  - Historic examples
- Generic DOE review
- Examples of the use of DOE
- Summary

Goals

- Describe the use of statistically designed experiments to assist the formulator to develop meaningful formulas
Formulation Principles

Before Formulation Start: Related Process and Management; Stage Gate or Similar Plan

- Depending on preferences, a coordinated business plan besides a formulation plan for a new product or process, an integrated plan is a wise choice
  - Many companies use a stage gate approach
  - Others will incorporate similar requirements but managers will run the program
- Choice of approach depends on
  - Culture
  - Magnitude
- But an integrated plan is a must
Formulating Perspective

- Needs on developing a formulation dictate direction of formulation and plan
- Experience can be a key component
  - A basic understanding of the technology base and how to formulate can short cut the whole development plan.
    - This depends on what is needed
    - Something out of the ordinary occurs
  - Recognizing preliminary screen results to decide what is next

Development Background

- Goal developed and clearly understood and integrated into a total plan
- Literature search
- Raw materials required
  - What are they? What do they do? Cost?
  - EH&S requirements -
- Test methods and equipment needed
Development: Technology Plan

- Write a technology project plan
  - Defines where to start project (goal)
  - Indicates where the end point is (success)
  - Provides a road map on how to get from start to finish

- The desired product is formulated
  - To meet the desired goal
  - Meet internal and external expectations
  - In concert with all concerned parties

- The process and product goes to commercialization

Historic Examples of DOE Use
Designed Experiments (DOE)

- DOE is not new
  - Before PC’s and even computers the concepts were formed
  - Main frame computers were used before PC’s
    - Same designs available
    - Punch IBM cards to enter data
  - PC’s to modern era
    - Software available to allow easier use of DOE
    - Newest Software very good with many options
- Software
  - Many options exist
  - Various degrees of utility

Paint Formulation

- The goal for the paint
  - Trade sales interior premium grade flat
  - Must have:
    - Excellent scrub and stain resistance
    - One coat hiding
- Investigated: existing formulations, raw materials understood, performance and tests
- DOE used to finish formulation (4 point with centroid point response surface on an IBM 360 mainframe)
- Result became a commercial product that sold many millions of gallons
Failed DOE - Resolving Plasticizer Performance Issue

- Problem - A resilient flooring foam layer viscosity with a new plasticizer product was extremely high and the rheology was bad.
  - This was not anticipated nor predicted
- Initial attempts to solve - One step at a time raw materials evaluated
  - This did not resolve the issue but insight to the formulation was gained
  - A mixture design seemed to be best option to solve
- The design was prepared, experiments executed and the software said the design produced lack of fits (not good)
- However one of the experiments looked really good and was the solution (Success!!!!)
- What happened? Basic incompatibility in the formulation caused unexpected issues. This lead to an understanding of the variables and a patent

Plastisol, Organisol Formulating with Solubility Parameters

- In US patent 8,034,860 Arendt discusses the use of solubility parameters to assist in formulating organisol and plastisols
- To achieve the viscosity, rheology and viscosity stability of a plastisol the overall solubility of the plasticizers and solvents used in the needs to be balanced
- It is not good to be right on the solubility parameter of the PVC but with a specified range of solubility parameters of the raw materials.
- It works with other considerations
A Sidebar- Use of Historic Data

- It is possible to use DOE software to use historic data
- There was an issue with quality at a plant I worked with: Too many lots of product were rejected because of being out of specification
- Question was were the specifications too tight?
- Used all the quality data for a year from the plant and the a response surface design (linear) was used to analyze
- Based on this analysis the specifications were changed and the changes the same or better quality
- Lots of money was saved (I did not get a big bonus. Just a thank you)

Generic Examples of DOE Used
Perspective

- The author and presenter is not an expert DOE consultant
- But I am an expert in formulating to solve problems
- Expert in plasticizers and several application areas
- The author and presenter gives results of his experiences in using designed experiments and his approaches
- Based on requirements it really is not always necessary to use a DOE approach
- But DOE's are a tremendous help when optimum's are required (or when an experienced formulator is stumped)
- There are excellent companies that design, train and sell software.

Formulating Approach

- Background
  - Understand raw materials key (all of them)
  - Basic performance understood
- Formulation development
  - Try to attain formulation performance with use understanding
  - Refine and confirm
  - If can not be done without significant data generation a DOE may be the answer
- DOE
  - Prepare a DOE design with the required design variables and response variables
  - Use a response surface, mixture design, combination, quadratic Optimal D or the like.
  - Test the “corners”
  - If all is good do the rest of the testing
  - Solve the need
Choices - Know Before Start

- One step at a time to define performance to the requirements.
  - Experience based formulation
  - Design does not require an in depth understanding
- Raw material evaluation
  - Drop new raw material into existing formulation and test
  - If it does not function as expected
    - Drop from further consideration
    - Reformulate based on experience
    - Use a DOE
- New formula
  - Start with a basic formulation
  - Develop performance requirements based on experience
  - Use a DOE to finish

Formulation Requirement

- Experimental design - Beyond the plan
  - One variable at a time testing is time consuming but appropriate for some projects
    - The type of project dictates use of one step at a time
    - Experience with technology key
  - Type of design to use?
    - A response surface or mixture design process can yield far more information to predict an optimal formulation
      - Need an understanding of the variables and test results
      - Need software and learn how to use
Generic Types of DOE Employed from Formulator Perspective

PC DOE Software

- Many choices - Minitab, JMP (Jump), Design-Expert® (Stat-Ease), E-Chip (Experimentation by Design) for example

- Design-Expert® 11 (and soon 12) software
  - Sold by Stat-Ease® Minneapolis, MN
    - Versatile, Easy to use, from Factorial to Mixture design
    - Much statistics for Scientists

- E-Chip® 7.0 software
  - Sold by Experimentation by Design
    - Very easy to use, less statistical in nature
    - Scientist Friendly
    - Newer releases unlikely unless to adjust to new OS
DOE Design Choices

- Types of designs
  - Factoral - To screen for significant variables
  - Response surface - Variables are continuous
    - Design Variables - What you are studying
    - Response Variables - What you need to understand changes in design variables
  - Mixture design - Truncated version of a response surface - For formulating
    - Variables same as above but all variables entered and all must equal one
    - Formulation ingredients are the design variables
    - Lots of possibilities in constraints
  - Combined designs
    - Mixture and response surface possible
    - Use of slack variables also possible

Response Surface and Mixture Design

- Used for process as well as formulation raw materials
- Design variables are continuous with appropriate response variables
- Several variables are possible as well as types of surfaces as well as designs
  - Generally two design variables are displayed but several are possible
  - Different types of representation to help understand the data developed and the trends
- The following next two slides indicate a design space and a full design
Examples of Generic Designs - Concepts Used by Presenter

The Figures in this next section were from Stat-Ease’s book *Formulation Simplified*. Written permission was obtained from Mark Anderson, one of the authors and principles of Stat-Ease. Design Expert 11 is the basis of this work.

Protocol - Replace Raw Material with Formulary Adjustments

1. Determined basis for design
2. Evaluated starting point formulation
3. Demonstrate the performance of the selected raw material in a fully formulated product
4. Determined key formulation variables and optimized using a DOE
Mixture Design: Simplex Centroid

Mixture Data
Cubic Results in 3D

Optimized Overlay
Truncated Mixture Design

Mixture Design: Truncated Triangle
DOE Specific Practical Use: Flexible Vinyl Formulating Examples

Publications

This is not the first rodeo for use of a computer to help formulation

  - Used a Simplex design, regression analysis
  - Looked at three design variables
  - Response variables were physical performance tests
  - Designed a general purpose filled compound and a high gloss hose compound

  - Program was developed to use plasticizer blends to replace a benchmark
  - Simplex response surface information was generated
  - Plasticizers at several levels were the design variables
  - Response variables: Physical performance parameters
  - With this design the authors were able to replace one plasticizer with a blend
Simplex Diagram of Composition Versus Application

DOE’s to Formulate in Flexible Vinyl: Some Aspect of Process or Physical Performance

Used by written permission of Len Krauskopf, President of Vinyl Consulting Co, Inc, From 2002 Vinyltec Seminar

X1 = Filler; X2 = PVC; X3 = Plasticizers
Goals and Formulation

- **Manufacturers**
  - Will have a particular goal or purpose for an evaluation
  - Goals
    - Reduce cost
    - New plasticizer (or blend)
    - New other raw materials than plasticizers
- **Raw material suppliers - Plasticizers**
  - A new plasticizer in the market is rare, but does happen
  - Different blends to specific requirements
  - Without a specific goal (What do plasticizer producers do? Well they do not sell products from theirs (well most of the time))
    - Create performance demonstrations
    - Use DOE’s to show performance
    - Create a data base and a program to dial in performance

Examples of Use of DOE’s: Flexible Vinyl Formulating
Papers with DOE

Examples of a supplier developing a plasticizer blend for two specific applications:

  - DOE on using new polymeric plasticizers
- Strepka, Arron, Arendt, William, Joshi, Makarand, “A Designed Experiment Approach to Optimizing the Performance of Benzoates and Phthalate Blends in Flexible Vinyl” SPE ANTEC 2007

SPE granted written permission to use the papers and figures in this presentation.

Optimizing Formulary for A New Polyester
Formulating with a New Polyester Plasticizer: Design

- A new polymeric plasticizer was designed for higher surface energy calendered films
  - Other raw materials affect surface energy
  - Need to provide formulation guidelines
  - DOE was selected to develop the guidelines
- EChip® 7 DOE software used to define experimental protocol
  - Response surface design was selected
  - A quadratic design, Optimal D selected

Variables

Variables

- Design - (one level of plasticizer used) variables
  - Heat stabilizers, ESO, lubricant, process aide
- Response - dynamic heat stability, static heat stability, Brabender torque values at equilibrium, high humidity compatibility, tensile properties, surface energy, and surface energy of aged film surface energy
Polymeric Design Charts

Aged Surface Energy

Dynamic Heat Stability

Polymeric Design Charts

High Temperature, Humidity Compatibility

Aged Surface Energy
Results of Study

- Based on the data produced from the design it was possible to design a next generation polymeric plasticizer
- Also while not a manufacturer of PVC goods sufficient data were generated to assist manufacturers of vinyl to properly formulate
- Interested in more detail?
  - Members of the SPE can download the whole article for free
  - Ask me
Study of Benzoate/Phthalate Blends in Resilient Flooring - Arendt et al

Resilient Flooring Construct - Study 1

- PUR Layer
- Wear layer
- Print
- Foam Layer
- Glass Felt/Saturation Layer
- Foam Layer
- Print
Benzoate/Phthalate Blends for Flooring Plastisol

It is not unusual to blend plasticizers to achieve performance

- When a high solvator such as a dibenzoate is needed to improve processing and other performance related requirements
- A study was conducted to provide answers on blends for a resilient flooring

- EChip® 7 DOE software utilized
  - A mixed design was used
    - A mixture design was selected for plasticizers
    - Optimal D with a quadratic model selected
    - Response surface used with a slake variable

Variables Defined

- Design variables – Mixed Design
  - Mixture design –
    - Plasticizers BBP, DINP, DIHP, Dibenzoate blend, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate
    - Plasticizers – 0 to 100%
    - TXIB – 0 to 20%
  - Response surface design variables
    - Dispersion resin
      - 70 to 100 PHR
    - Slack variable, dispersion resin
      - 0 to 30 PHR
  - Response Variables
    - Plastisol viscosity and rheology; Gel/fusion; Tensile; Hardness; Volatility; Staining; Plastisol stability; heat stability UV stability
Rheology Chart

Plastisol Blend Charts
Results of DOE

- There is no doubt that the study is dated from a perspective of what was studied and the raw materials used.
- However the approach is sound and did provide answers that were required
- If the article is of interest it is available to SPE members free of charge

Study of Benzoate/Phthalate Blends in Resilient Flooring - Strepka et al
Flooring Construct - EU basis for this study - Study 2

- PUR Layer
- Clear layer
- Print
- Top Foam Layer
- Glass Felt with Saturation Layer
- Bottom Foam Layer
- Print

Benzoate/Phthalate Blends for Flooring Plastisol
Blends of plasticizers are used to achieve performance and alternates to achieve performance goals are sought

- When a high solvator such as a dibenzoate is needed to improve processing and other performance related requirements
- A study was conducted to provide answers on blends for a resilient flooring with alternate methods to control performance compared to previous studies

- Design-Expert® and EChip® software utilized
  - A mixture design was selected
  - Optimal D with a quadratic model selected
Variables

- Design variables
  - Mixture design - Plasticizers DINP, Triethylene glycol, diethylene glycol and dipropylene glycol dibenzoate blend, diluent types 2-ethylhexyl benzoate and 2-ethylhexyl laurate.
    - DINP - 40 to 75%, 2EHB - 0 to 35%, Dibenzoate blend 10 to 60%, 2EHL 0 to 2.5%
  - Response variables - Plastisol - Viscosity, Degassing, Gel/fusion temperatures, Fused vinyl Tensile properties, Stain resistance properties, Shore A durometer

Reading the Triangle
Mixture Design

Plastisol Stability Graphed
Design

When a high solvating plasticizer is used in a plastisol formulation even in a blend:

- Plastisol viscosities will be higher than if only a GP type plasticizer is used.
- But a GP type will not process as fast as a high solvator.
- The challenge is always to get the best balance of performance

The experiment indicated other ways than presented earlier to achieve the required balance

Refer to the paper (it is free to SPE members). The full design is published.
Recap

- The basic principles of formulating:
  - Know the goal
  - Develop an understanding of requirements and what has been done
  - Prepare
  - Plan
  - Execute
- Start experiments to gain an understanding
- Use designed experiments
  - With basic knowledge it is the best way
  - Refine as necessary

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  - Formulating with Plasticizers
  - Formulation Basics
Bibliography

- Anderson, Mark, Whitcomb, Pat, Bezener, Martin, *Formulation Simplified*, Routledge, Taylor & Francis, NYNY, 2018
- Neuman, Richard, *Experimental Strategies for Polymer Scientists and Plastics Engineers*, Hanser Publishers, Germany, 1997 (SPE)
- Box, G, Hunter, W., Hunter, S. *Statistics for Experimenters*, John Wiley and Sons, NYNY, 1978

Bibliography

- “Use of Dibenzoate Plasticizers in Pressure Sensitive Adhesives”, Arendt, William; McBride, Emily; Conner, Marianne; PSTC Tape Summit, New Orleans, LA, May 13 to 17, 2013.
Bibliography

- Fibiger, W., Boyce, A.C., Book II. Trade Sales and Architectural Coatings, ITE Consultants, 1995
  - Chapter VIII - Formulating Latex Paint
  - Chapter IX - Special Formulating Know How


- “Optimization of Silyl Terminated Polyether Sealants Based on Dibenzoate Plasticizers”, William Arendt, Gina Johnson, Emily McBride, FEICA 2016 conference, September 7 to 9, 2016, Vienna Austria.

Bibliography

Questions?

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