Rubber Division of ACS
183 Spring Meeting
Akron, OH, April 24. 2013

New Tool for a Systematic Development and Improvement Of Compounds

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Content of Presentation

- Introduction
- Tools in Compound Development
- Motivation for Program Development
- What is the GrafCompounder?
- Comparison with Statistic Experimental Design (DoE)
- Combination of GrafCompounder with DoE
- Advantages / Summary

Introduction

Recipe is used 1 Time per Project / Evaluation

**Reinvention Time*)
~ 1- 2 Jahre!**

) personal Estimation

**Mid size - / Large company:
Recipes in use ~ 500 – 2000
Laboratory recipes ~ 1000/year**

***Cost of Recipe Development in a Laboratory
~ 500 US$/Recipe
=
Invest of 500.000 US$/year***

Introduction

Question:

- Why we can hardly take compound databases as working capital, Saving time and effort in our daily work?
  - Avoiding reinvention
  - Increase our compounding knowledge.
  - Gaining room for really new ideas in compound development

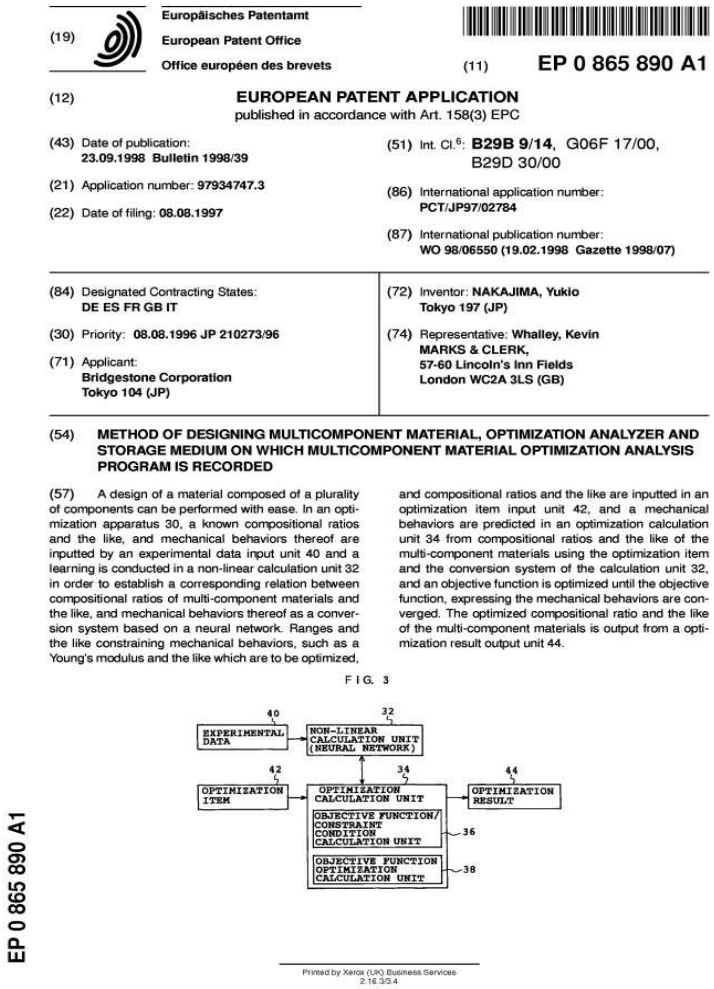
- A compound database is a kind of happenstance data and not suitable for analysis of ingredient – property dependencies

Introduction

- **Program developments and patents dealing with “Neuronal Network Algorithm” to create recipes from compound databases.**
  - **US 7451122 Empirical DoE / Honeywell / 2008**
  - **US 7158672 Matt Colour Shades / DuPont 2007**
  - **US 2005/0160114 2005 Similarity of Recipes / TDHunt 2005**
  - **US 6714924 Colour Match Formulation / BASF 2004**
  - **WO03/069516 Multi - Component Composition / GE 2003**
  - **US 6671661 Bayesian Component Analysis / Microsoft 2003**
  - **US 6411945 Multi Component Material / Bridgestone 2002**
  - **WO 99/50770 Search Virtual Libraries / CombiChem 1998**
  - **US 4979126 Non Linear Transformation / AI Ware 1990**
  - **US 3781909 Colour Match / American Cyanamid 1973**

Introduction

- **Patent EP 0865 890 A1 (Bridgestone) is dealing with compounds used in tire manufacturing**
  - **Dependency of factor – response relationship with none linear regression equation.**
  - **Usage of a function to determine boundary conditions.**
  - **Identification of a compound with targeted properties.**



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 865 890 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
23.09.1998 Bulletin 1998/39

(21) Application number: 97934747.3

(22) Date of filing: 08.08.1997

(51) Int. Cl.[6]: B29B 9/14, G06F 17/00, B29D 30/00

(86) International application number:
PCT/JP97/02784

(87) International publication number:
WO 98/06550 (19.02.1998 Gazette 1998/07)

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: 08.08.1996 JP 210273/96

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(54) METHOD OF DESIGNING MULTICOMPONENT MATERIAL, OPTIMIZATION ANALYZER AND STORAGE MEDIUM ON WHICH MULTICOMPONENT MATERIAL OPTIMIZATION ANALYSIS PROGRAM IS RECORDED

(57) A design of a material composed of a plurality of components can be performed with ease. In an optimization apparatus 30, a known compositional ratios and the like, and mechanical behaviors thereof are inputted by an experimental data input unit 40 and a learning is conducted in a non-linear calculation unit 32 in order to establish a corresponding relation between compositional ratios of multi-component materials and the like, and mechanical behaviors thereof as a conversion system based on a neural network. Ranges and the like constraining mechanical behaviors, such as a Young's modulus and the like which are to be optimized, and compositional ratios and the like are inputted in an optimization item input unit 42, and a mechanical behaviors are predicted in an optimization calculation unit 34 from compositional ratios and the like of the multi-component materials using the optimization item and the conversion system of the calculation unit 32, and an objective function is optimized until the objective function, expressing the mechanical behaviors are converged. The optimized compositional ratio and the like of the multi-component materials is output from a optimization result output unit 44.

FIG. 3

EP 0 865 890 A1

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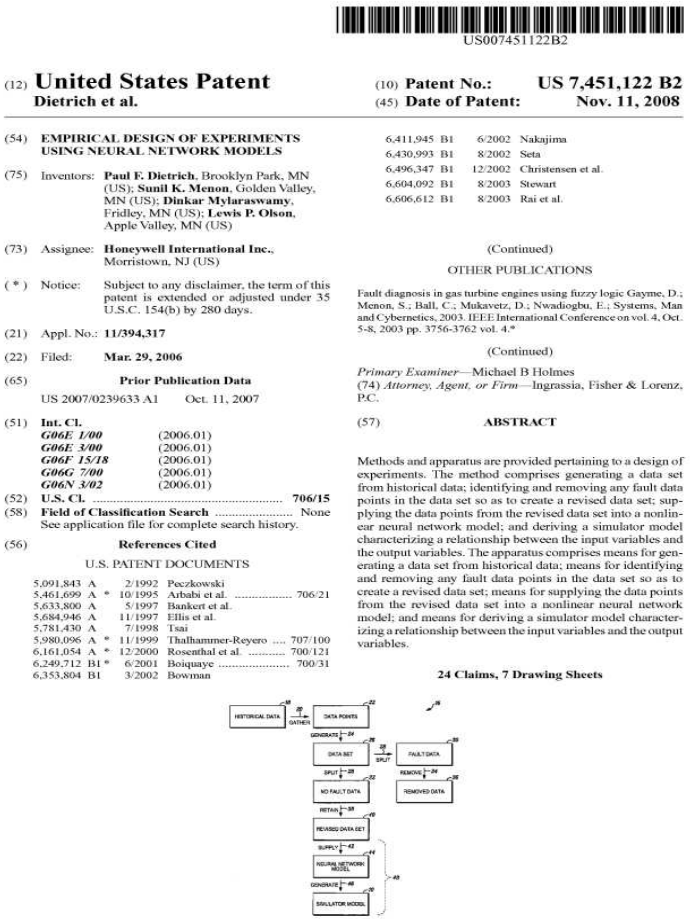
2.16.3/3.4

Introduction

- **The patent US 7541122B2 (Fa. Honeywell) deal with „empirical“ DoE with the help of neuronal network algorithm**
  - **Datenbase from historical compound data**
  - **Elimination of foulty data out of the data base**
  - **Calculation of a compound with the help of none linear neuronal network algorithm**
  - **Building of a equation for the simulation of the correlation between factors (compound ingredients) and responses (properties).**



US007451122B2

(12) **United States Patent**
Dietrich et al.

(10) **Patent No.: US 7,451,122 B2**
(45) **Date of Patent: Nov. 11, 2008**

(54) **EMPIRICAL DESIGN OF EXPERIMENTS USING NEURAL NETWORK MODELS**

(75) Inventors: **Paul F. Dietrich**, Brooklyn Park, MN (US); **Sunil K. Menon**, Golden Valley, MN (US); **Dinkar Mylaraswamy**, Fridley, MN (US); **Lewis P. Olson**, Apple Valley, MN (US)

(73) Assignee: **Honeywell International Inc.**, Morristown, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 280 days.

(21) Appl. No.: **11/394,317**

(22) Filed: **Mar. 29, 2006**

(65) **Prior Publication Data**

US 2007/0239633 A1 Oct. 11, 2007

(51) **Int. Cl.**

G06E 1/00	(2006.01)
G06E 3/00	(2006.01)
G06F 15/18	(2006.01)
G06G 7/00	(2006.01)
G06N 3/02	(2006.01)

(52) **U.S. Cl.** **706/15**

(58) **Field of Classification Search** ..... None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,091,843	A	2/1992	Peczkowski	
5,461,699	A *	10/1995	Arbabi et al.	706/21
5,633,800	A	5/1997	Bankert et al.	
5,684,946	A	11/1997	Ellis et al.	
5,781,430	A	7/1998	Tsai	
5,980,096	A *	11/1999	Thalhammer-Reyero	707/100
6,161,054	A *	12/2000	Rosenthal et al.	700/121
6,249,712	B1 *	6/2001	Boiquaye	700/31
6,353,804	B1	3/2002	Bowman	
6,411,945	B1	6/2002	Nakajima	
6,430,993	B1	8/2002	Seta	
6,496,347	B1	12/2002	Christensen et al.	
6,604,092	B1	8/2003	Stewart	
6,606,612	B1	8/2003	Rai et al.	

(Continued)

OTHER PUBLICATIONS

Fault diagnosis in gas turbine engines using fuzzy logic Gayme, D.; Menon, S.; Ball, C.; Mukavetz, D.; Nwadiogbu, E.; Systems, Man and Cybernetics, 2003. IEEE International Conference on vol. 4, Oct. 5-8, 2003 pp. 3756-3762 vol. 4.*

(Continued)

Primary Examiner—Michael B Holmes
(74) *Attorney, Agent, or Firm*—Ingrassia, Fisher & Lorenz, P.C.

(57) **ABSTRACT**

Methods and apparatus are provided pertaining to a design of experiments. The method comprises generating a data set from historical data; identifying and removing any fault data points in the data set so as to create a revised data set; supplying the data points from the revised data set into a nonlinear neural network model; and deriving a simulator model characterizing a relationship between the input variables and the output variables. The apparatus comprises means for generating a data set from historical data; means for identifying and removing any fault data points in the data set so as to create a revised data set; means for supplying the data points from the revised data set into a nonlinear neural network model; and means for deriving a simulator model characterizing a relationship between the input variables and the output variables.

24 Claims, 7 Drawing Sheets

Introduction

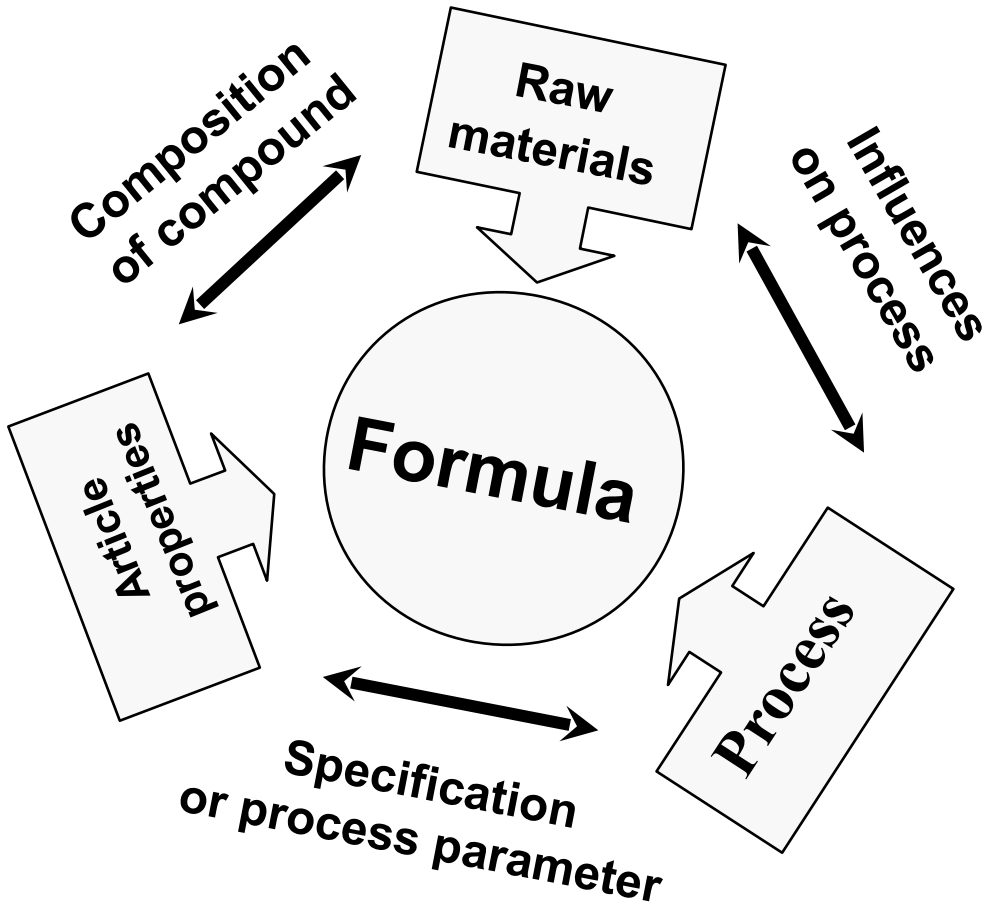
- **Program for Compound Development / Simulation**
  - **None of such or similar program is available on the market**
  - **One Program was tested in the late 90ties**
    - **It needed a huge database, which was created with compounds manufactured and tested in laboratory scale**
    - **It failed to accurate predict a compound**
    - **Later is was taken from the market**
  - **There is no tool to work with a database, except**
    - **Search with a Program like Access® or similar**
    - **Working with the Solver in Excel®**
    - **Integrated Solution in Laboratory Information Management Systems (LIMS)**

Tools in Compound Development

- **Which methods are used?**
  [It is always about the effect of one/more ingredient(s) on a result / a response]
  - **Trial and error**
  - **Repetition of an experiment**
  - **Change of an existing compound through (One Factor a Time)**
    - **Gradual change of a factor**
    - **Relative change of two factors to each other**
    - **Blending of mixtures!**
  - **Analysis with the help of correlation and regression**
    - **Pareto analysis**
    - **Cause effect diagrams**
  - **Statistic experimental design technology (DoE)**
    - **Latin square test approaches**
    - **Factorial designs approaches**
  - **Variance analysis**

Tools in Compound Development

- **Method tool box**
  - **Blending of mixtures**
  - **Simple set of experiments**
  - **Experimental test designs**
    - **Statistical Design of Experiment (DOE)**
  - **Database analysis**



Tools in Compound Development

- **Reference mixture and variation (OFAT: One Factor a Time)**

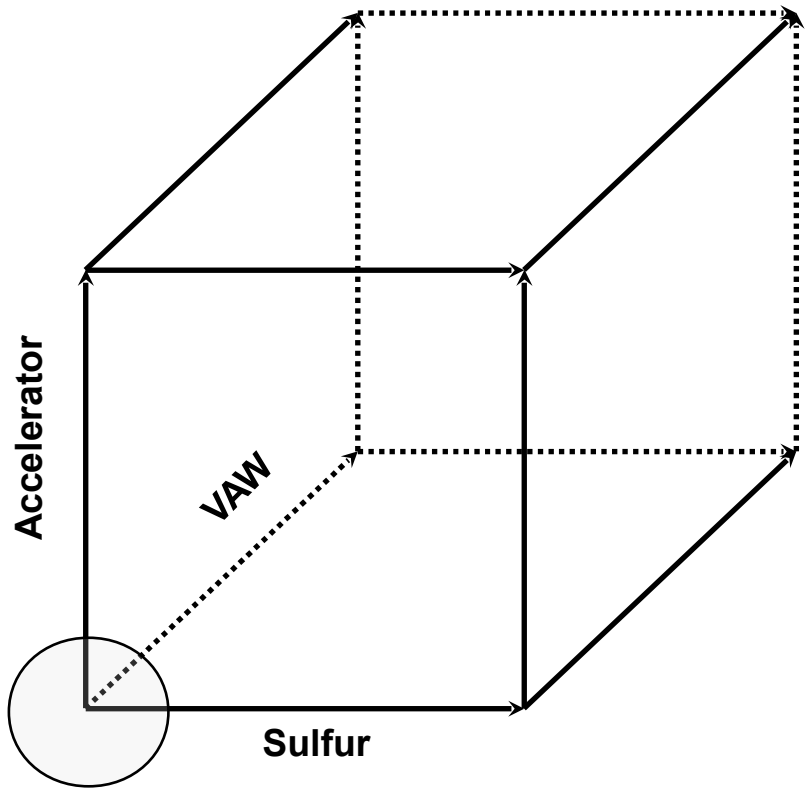
- **Disadvantages of this method:**
  - **Interactions are ignored**
  - **Ignoring of statistical noise, if tests repeated.**
  - **Causes high effort because to many iterations necessary over a greater period of time**
    - *possible, but no confidence about repeatability* -
    achieving the target on the long run.

Tools in Compound Development

- **Statistic Experimental Design**
  Experimental setup with known compound as a starting point

- **Base compound / Accelerator investigation**
  - Sulfur amount
  - Accelerator
  - Process aid

- **Advantages**
  - Randomization
  - Repetitions
  - Ingredients are varied against each other in steps
  - Plan is completed and evaluation statistically sound. (Latin square)
  - Noticing additional repetitions of the central point.

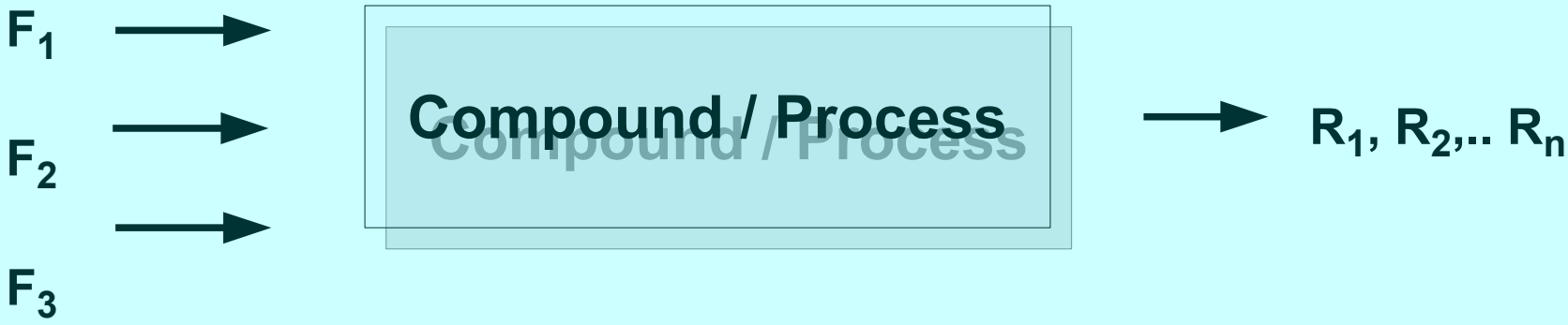


Tools in Compound Development

Statistic Experimental Design (DoE) allows a factor – response calculation with regression equations

Influences:
Factors are varied

Effects:
Responses are measured

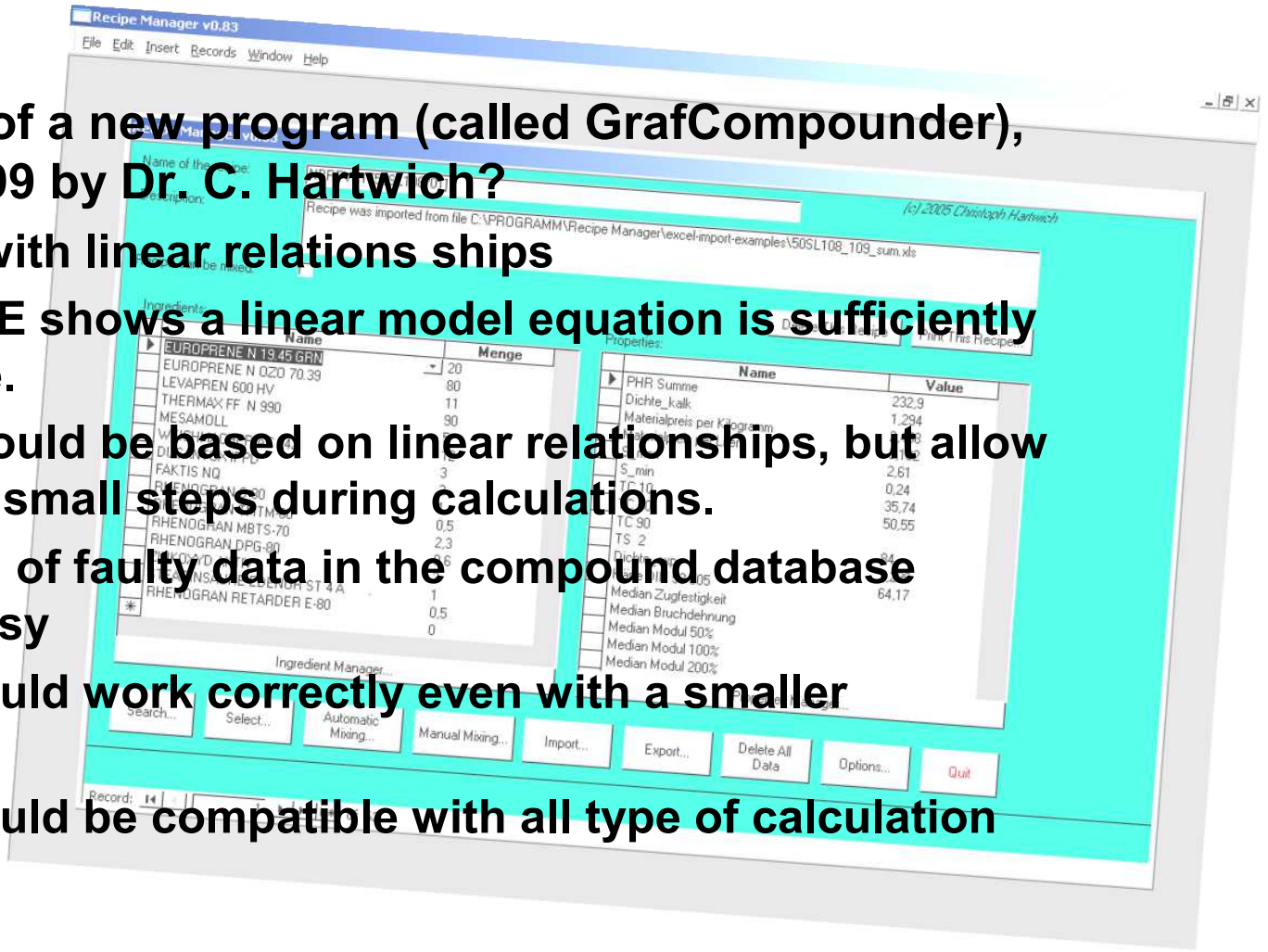


Objective of the Experiment should be the identification of the most important factors (F_1,..F_n), to be able to measure Effects (Responses R_1,...R_n) and to describe there dependency in a mathematical equation:

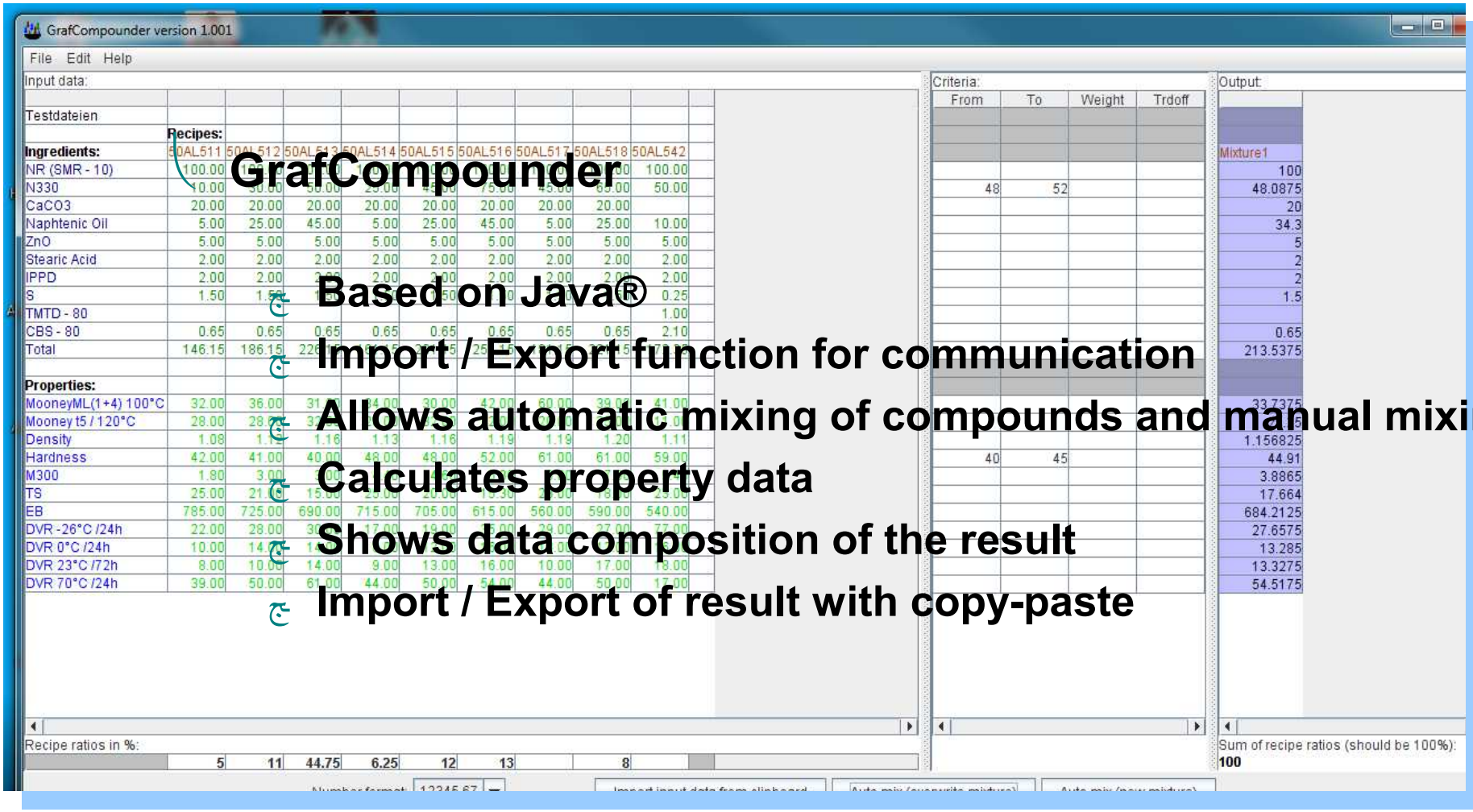
$$R_{i(1...n)} = f(A_0 + A_1F_1 + ...A_nF_n + ...)$$

GrafCompounder

- What is the aim of a new program (called GrafCompounder), developed in 1999 by Dr. C. Hartwich?
  - Calculation with linear relations ships
    - Most DoE shows a linear model equation is sufficiently accurate.
    - Math should be based on linear relationships, but allow multiple small steps during calculations.
  - Identification of faulty data in the compound database should be easy
  - Program should work correctly even with a smaller database
  - Program should be compatible with all type of calculation programs



GrafCompounder



- GrafCompounder
- Based on Java®
- Import / Export function for communication
- Allows automatic mixing of compounds and manual mixing
- Calculates property data
- Shows data composition of the result
- Import / Export of result with copy-paste

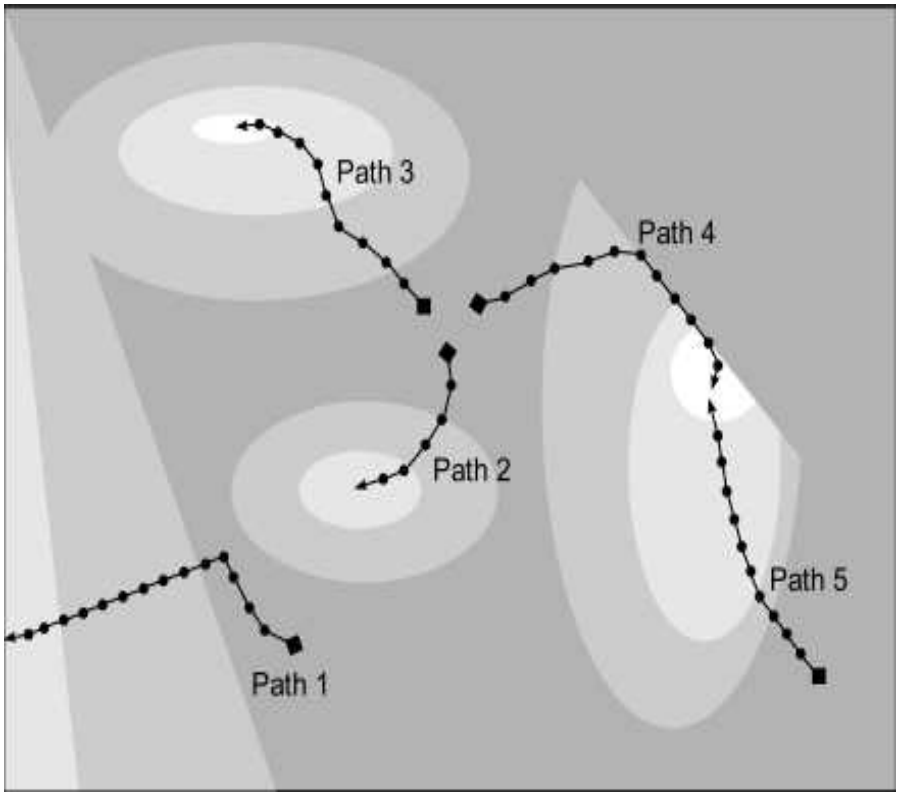
GrafCompounder

- **Analysis of a recipe database with Multiple Linear Iteration (MLI)**
  - **Search criteria manageable with different weights!**
  - **Recipe selection (Exclusion of unwanted recipes during analysis)**
    - **Avoid analysis of compounds based on none compatible polymers**

      (*Because of possible none linear effects due to influence of phase morphology on properties*)
  - **Automatic and manual mode**
    - **Simulation of blending compounds selected by the operator**
  - **Property data should be from a trustworthy source, if not your own**

GrafCompounder

- **Analysis based on**
  - **Measurables**
  - **Targets**
  - **Weights**
  - **Rating functions shows the distance between values and target**
  - **Iteration in small steps from different starting points**
  - **Check of maximum agreement with the target**
- **Report of Results**
  - **Recipe**
  - **All calculable physical properties**
    - **Missing data left out**
  - **Show all Recipes with their percentage used in an analysis**



GrafCompounder

- **Working with the GrafCompounder**
  - **Create a table by copy/paste from Design Expert®**
  - **Assign titles to the rows and columns with:**
    - **Recipes:**
    - **Ingredients:**
    - **Properties:**

	Recipes:		
Ingredients:	CMPD1	CMPD2	CMPD3
xxx	xxx	xxx	xxx
Properties:			
xxx	xxx	xxx	xxx

Comparison of
DoE with GrafCompounder

- **Testing the MLI-method a database is needed, which can be analyzed in different ways.**
  - **1. Example**
    - **Oil / Filler DoE (with own experiments)**
    - **Factors: Filler 1, filler 2, filler3 and oil**
  - **2. Example**
    DoE published by DuPont Dow in 1998
    - **Factors: ENB, DTDC, S, MBT, TiTBD, ZdiBC, DTP**
  - **Same optimization criteria will be used in DoE software (Design Expert®) and in GrafCompounder.**

Comparison of
DoE with GrafCompounder

- **1. Example**
  - **Oil / Filler DoE (based on own experiments)**
  - **Factors: Filler 1, Filler 2, Filler 3 and Oil**

Comparison of
DoE with GrafCompounder

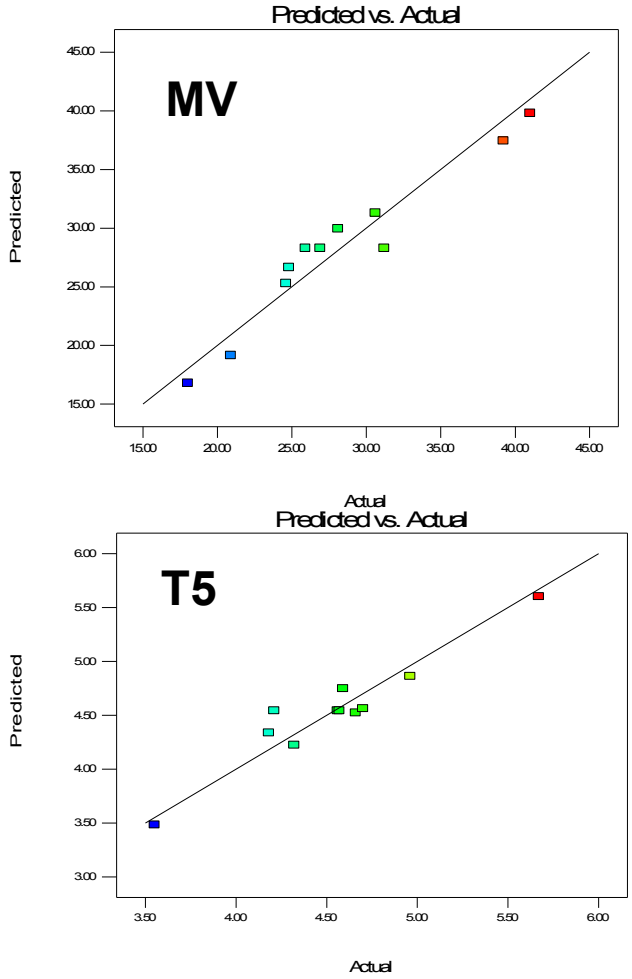
- DoE with 4 Factors
  Polymer used was Vistalon® 8600
- Factor Name Units Minimum Maximum
  - A C6630 phr 60.00 95.00
    B CaCO3 phr 10.00 70.00
    C Clay phr 10.00 50.00
    D Oil phr 70.00 95.00

  - A fractional factorial DoE with 11 compounds only!

Comparison of
DoE with GrafCompounder

- **Rheological Data are examined**
  - **MV and T5 can be measured quite accurate.**

    Both are significant with a linear model equation

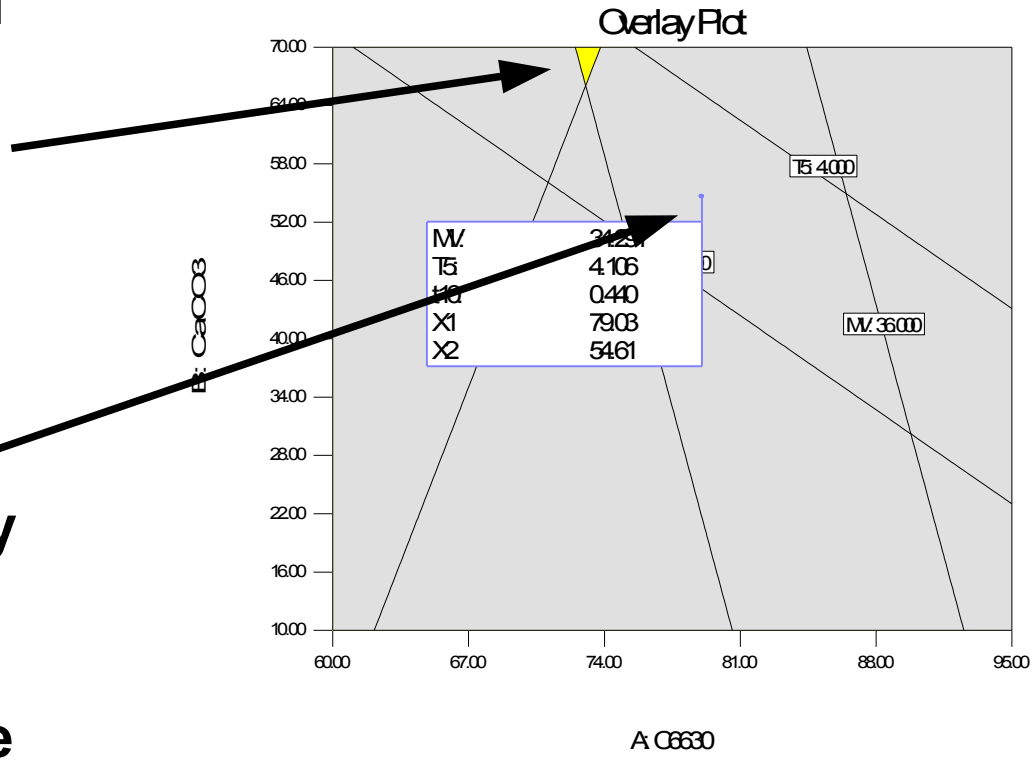


Comparison of
DoE with GrafCompounder

Ingredients	Unit	DoE Optimization	GrafCompounder
CB 6630	phr	73	79
CaCO3	phr	68	55
Clay	phr	39	39.5
Paraffinic Oil	phr	72	73
MV 120	MU	34	34.9
T5 (120°C)	min	4.04	4.2
t10 (170°C)	min	0.45	0.44

Comparison of
DoE with GrafCompounder

- Optimization area calculated with Design Expert®
- Solution given by GrafCompounder



- With the additional boundary condition:
  Same amount of CB 6630 similar to Optimization Value in Design Expert®

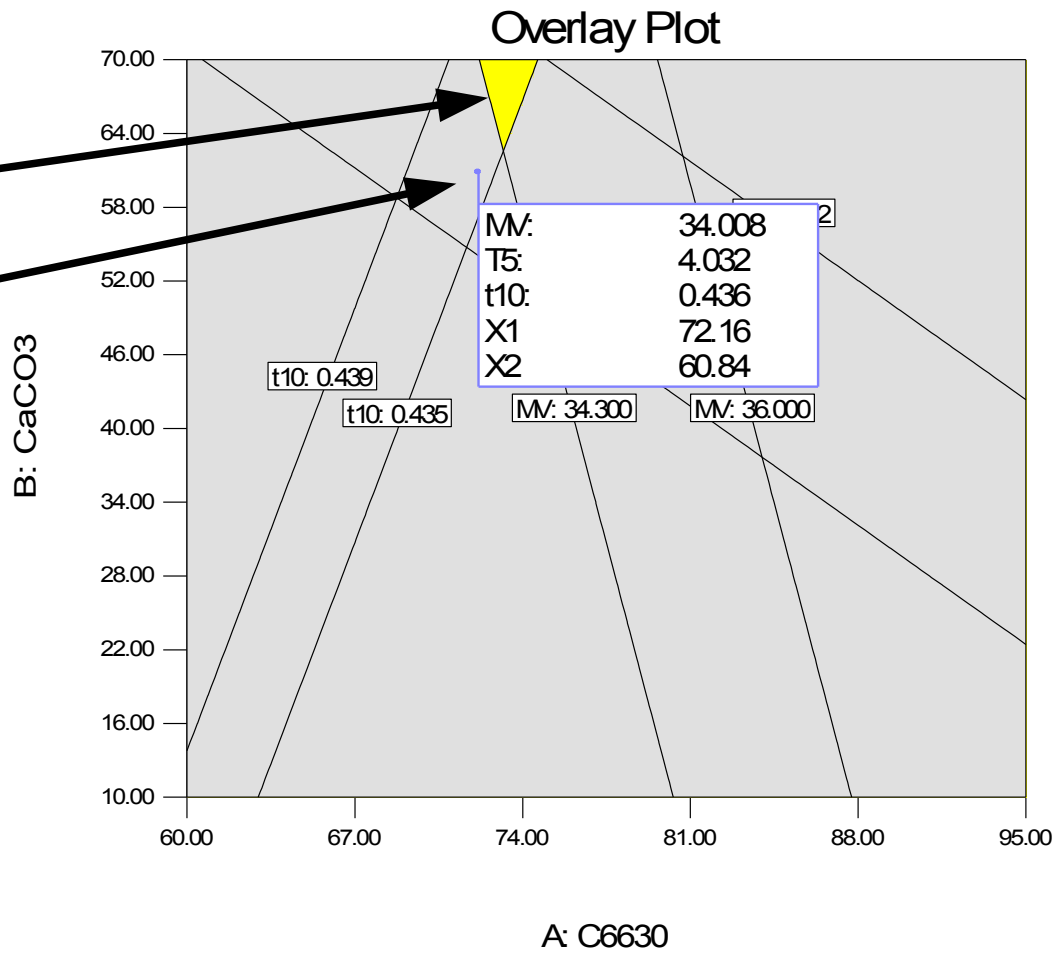
Comparison of
DoE with GrafCompounder

Ingredients	Unit	DoE Optimization	GrafCompounder
CB 6630	phr	73	73
CaCO3	phr	68	61
Clay	phr	39	32
Paraffinic Oil	phr	72	70
MV 120	MU	34	34.1
T5 (120°C)	min	4.04	4.1
t10 (170°C)	min	0.45	0.45

Comparison of
DoE with GrafCompounder

- **Optimization area calculated with Design Expert®**
- **Solution given by GrafCompounder**

  with the additional condition (CC 6630 – 73 phr)



Comparison of
DoE with GrafCompounder

Ingredients	Unit	DoE Optimization	GrafCompounder	DoE Point Prediction
CB 6630	phr	73	73	73
CaCO3	phr	68	61	61
Clay	phr	39	32	32
Paraffinic Oil	phr	72	70	70
MV 120	MU	34	34.1	34.2 ± 3
T5 (120°C)	min	4.04	4.1	4.01 ± 0.25
t10 (170°C)	min	0.45	0.45	0.43 ± 0.07

Comparison of
DoE with GrafCompounder

- What we have learned from previous Experiment?
  - Calculation with GrafCompounder and optimization result with Design Expert has some characteristic differences
    - GrafCompounder gives always one solution
    - DoE with Design Expert® provides an area, where you can identify a solution
    - With an additional boundary condition both solutions can be narrowed, that they fit into 95% confidence interval and measurement error of test methods for the responses.

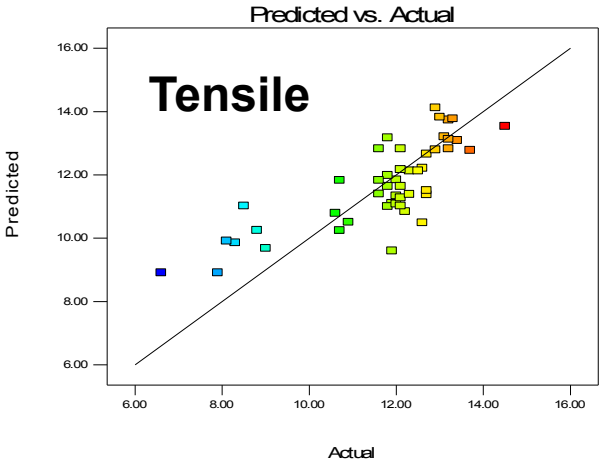
Comparison of
DoE with GrafCompounder

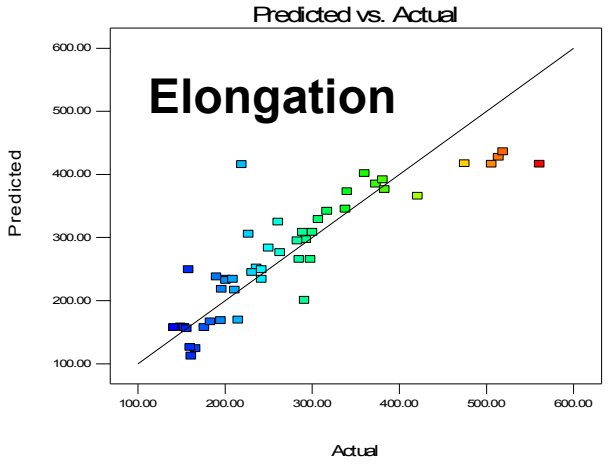
2. Example

- DoE published by DuPont Dow in 1998
  - Factors: ENB, DTDC, S, MBT, TiTBD, ZdiBC, DTP
  - DoE with 41 Experiments

Comparison of
DoE with H-JGCompounder

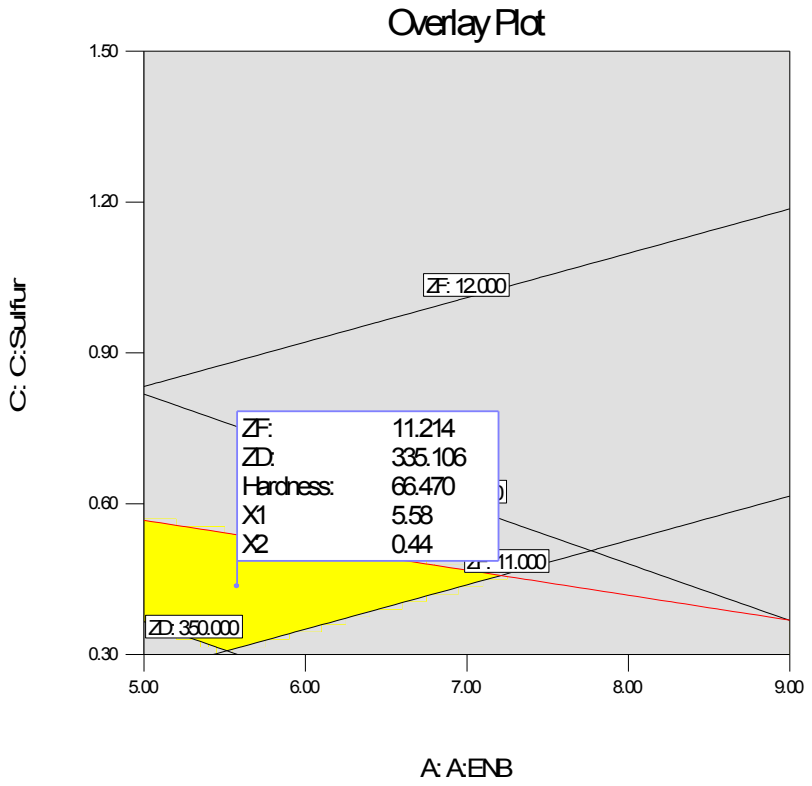
- **Tensile at break is significant with linear model**
  - **Sulfur has larger influence followed by DTDC and TiBTD, but negative**
- **Elongation is significant with quadratic model, but linear model is a sufficient fit**
  - **Sulfur has the largest influence followed by DTDC**
- **Hardness is sufficient significant with linear model as well**
  - **Main influence: Sulfur, DTDC**





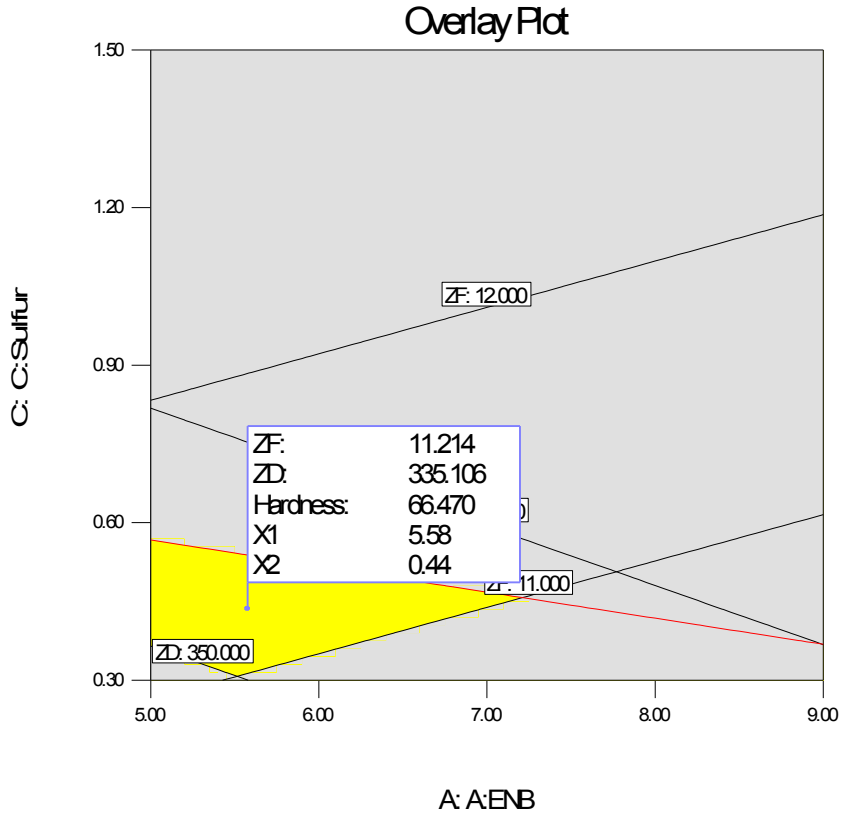
Comparison of
DoE with GrafCompounder

- **Selection of responses for the test with graphical optimization:**
  - **Hardness**
    65°ShA - 70°ShA
  - **Tensile at break**
    11MPa – 12 MPa
  - **Elongation of Break**
    350 % - 400 %
- **Flag points to desirable solution**



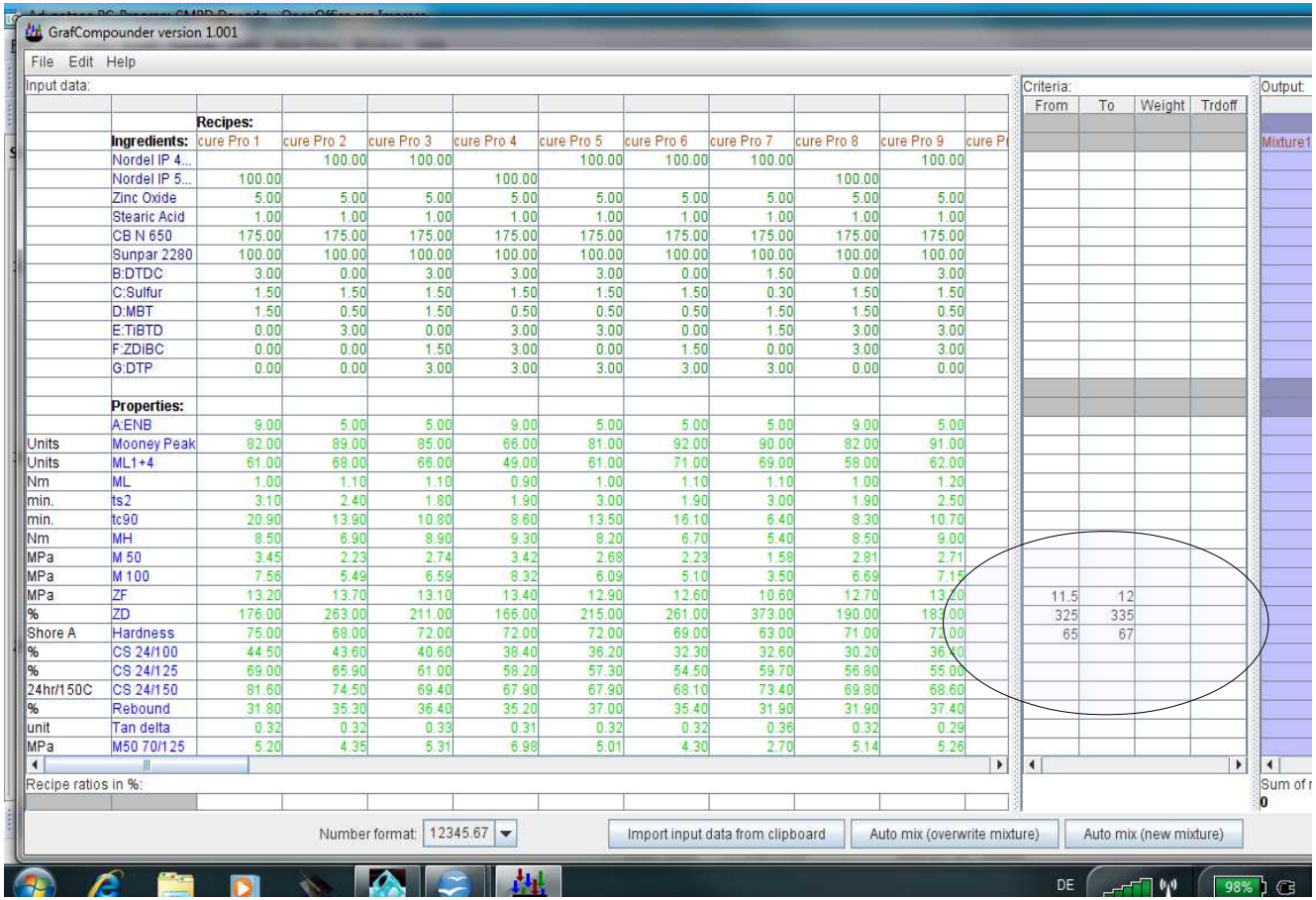
Comparison of
DoE with GrafCompounder

- **Factor values yielding this result**
  - **ENB: 5,58%**
  - **Sulfur – 0.44 phr**
  - **DTDC – 2.11 phr**
  - **MBT – 1.00 phr**
  - **TiBTD – 1.50 phr**
  - **ZdiBC – 1.50 phr**
  - **DTP – 1.50 phr**



Comparison of
DoE with GrafCompounder

- **Paste table with all data into GrafCompounder**



Comparison of
DoE with GrafCompounder

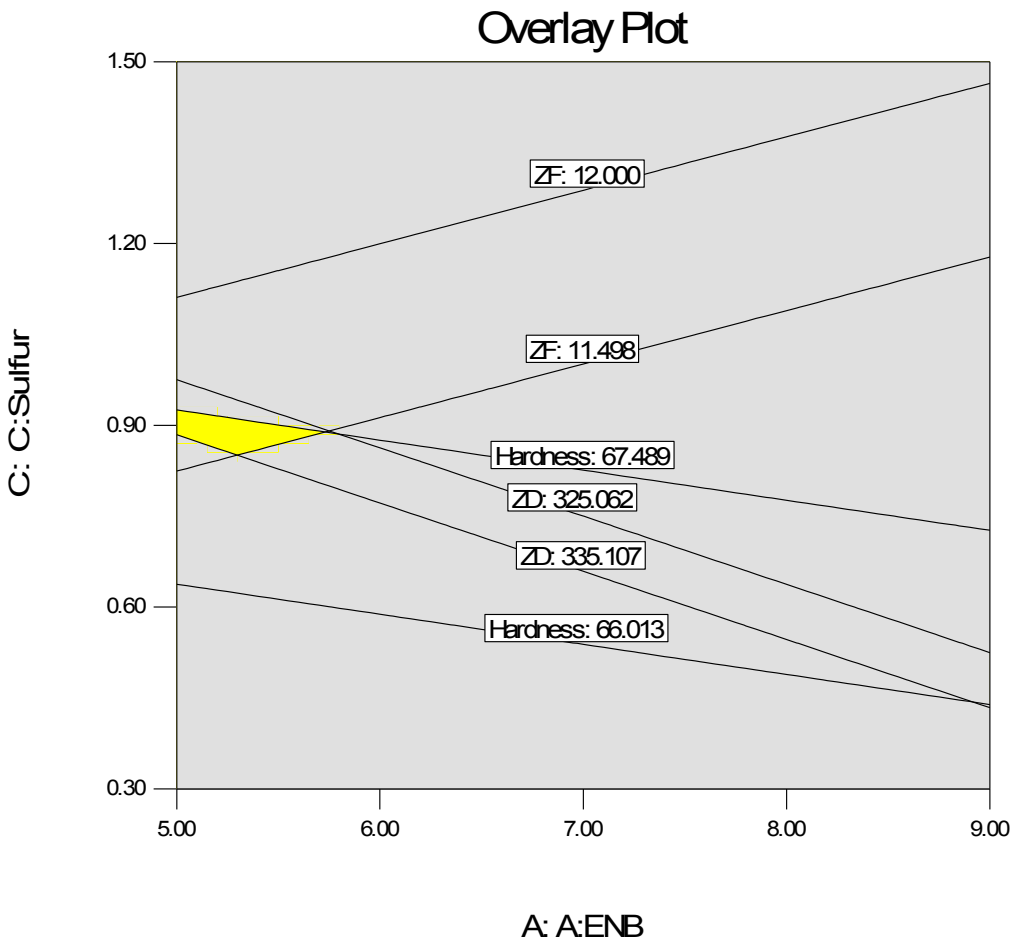
- **Paste table into GrafCompounder**

  - **ZF-MPa : 11.5-12.0**
  - **ZD-% : 325-335**
  - **H-°ShA : 65-67**

Ingredients	Result
A: ENB	**6.5**
B:DTDC	**0.98**
C:Sulfur	**0.93**
D:MBT	**1**
E:TiBTD	**1.51**
F:ZDiBC	**1.33**
G:DTP	**1.45**
ZF	**11.5**
ZD	**325**
Hardness	**67**

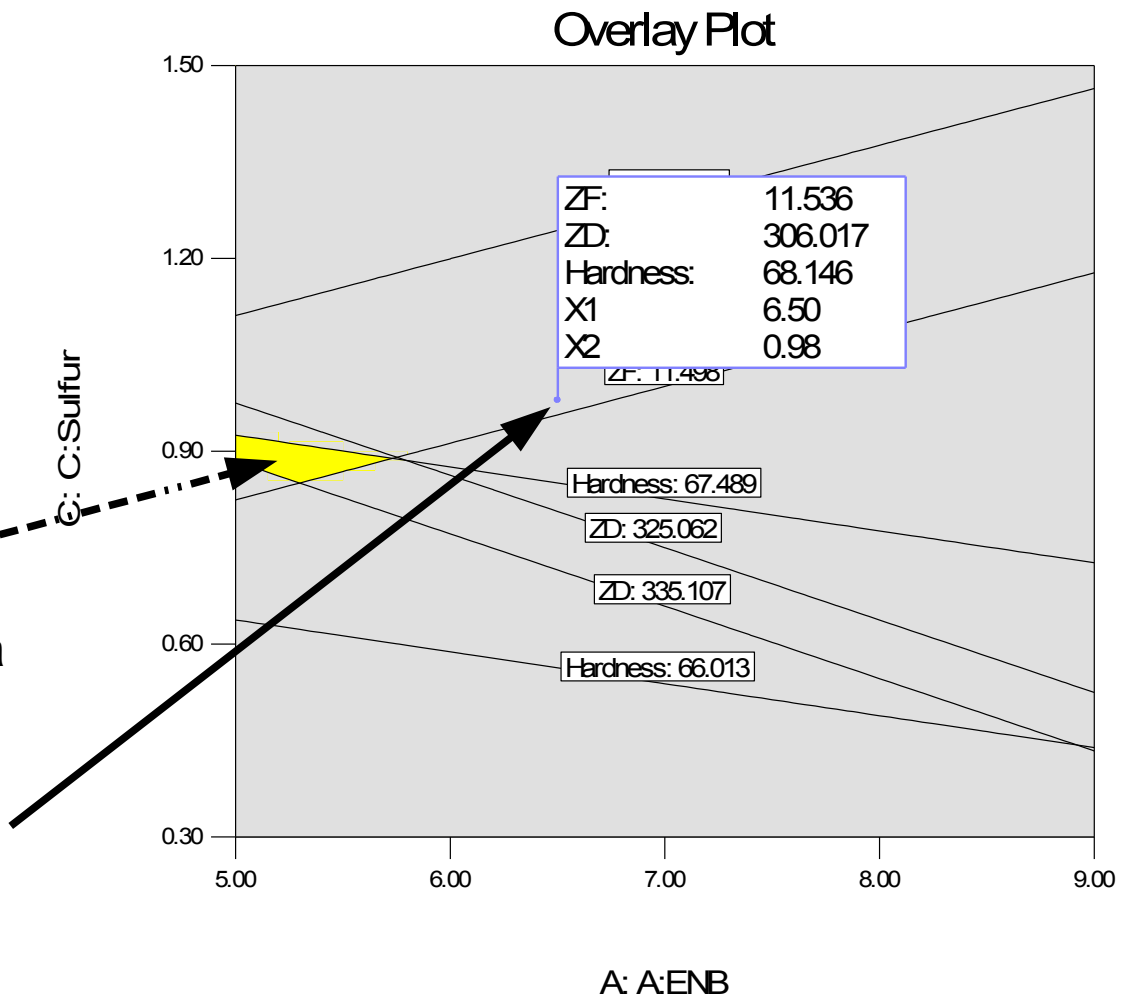
Comparison of
DoE with GrafCompounder

- **Run Optimization Graphical**
  - **ZF-MPa : 11.5-12.0**
  - **ZD-% : 325-335**
  - **H-°ShA: 65-67**



Comparison of
DoE with GrafCompounder

- **Boundary Conditions**
  - **ZF-MPa : 11.5-12.0**
  - **ZD-% : 325-335**
  - **H-°ShA : 65-67**
- **The Design Expert® optimization graph shows the location of the result as a yellow area, but GrafCompounder result is tagged with a flag.**



Comparison of
DoE with GrafCompounder

Boundary Conditions

- **ZF-MPa : 11.5-12.0**
- **ZD-% : 325-335**
- **H-°ShA : 65-67**

Ingredients	Result GrafCompounder	Result Design Expert®
ENB	**6.5**	**5.45**
C:Sulfur	**0.93**	**0.88**
B:DTDC	**0.98**	**0.98**
D:MBT	**1**	**1**
E:TiBTD	**1.51**	**1.51**
F:ZDiBC	**1.33**	**1.33**
G:DTP	**1.45**	**1.44**
ZF	**11.5**	**11.5**
ZD	**325**	**330**
Hardness	**67**	**67.5**

+) Note: Accelerators are preset!

Comparison of
DoE with GrafCompounder

What is the lesson learned?

- There are characteristic differences between the calculation of compound properties with the prediction tool of a DoE program and a compound simulation program based on MLI
  - The differences depend on the correlation factor and the statistic model equations used for calculation
  - The differences are inside a 95% confidential interval
  - They are inside the measurement error of processes and methods used in the rubber industry.

Simulation of
DoE with GrafCompounder

- **Ingredients selection with GrafCompounder**
  - **Database should be sufficient large**
  - **Ingredients and limits according DoE software**
    - **Run or standard order: both is possible**
    - **Create recipes/properties with GrafCompounder**
    - **Mix and test compounds in the laboratory**
    - **Compare “Simulated” design with executed design**
    - **Correlation analysis (ANOVA) of simulated and experimental compounds with DoE Software**
    - **Fold both DoE Data and analyze, whether correlation coefficient becomes smaller**
  - **Keep your database organized!**

Conclusion

- **GrafCompound Simulator**
  - **Creation of a formula according predefined criteria**
    - **Ingredients**
    - **Properties**
  - **Traceability to the starting formulas**
    - **Analysis of outliers and their correction or elimination in the database is possible.**
    - **Integration of results from statistical experimental designs.**
    - **Inquiry of databases of different origin, provided that an export of the data is possible with all known Office programs.**
- **Result of the calculations MUST be confirmed by an experiment.**
  - **Probability of a match between calculation and confirmation experiment result is about 90-5% according first experience**

Conclusion

- Compounds in databases are type of happen stance data
  - Which can not analyzed with a systematic approach today
  - DoE in each case needs data based on a planned experiment.
- GrafCompounder allows to search a database for a possible solution using targets
  - At minimum you get an very good idea about the centre point in a DoE

Thank you for your attention.

Any questions?

Any comments?

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