My First DOE

Disclaimer

The photographic products described here are obsolete, but the technical details of product design are still considered proprietary. The chemicals are described in generic terms. The numbers are expressed in design units. The effects are a loose approximation of the actual results.

Background

I was a young engineer at Eastman Kodak working on an automated processing machine for super 8 movie film. The plastic cartridge that held the film was generating lots of static that caused blue blotches and lightning bolts on the exposed film. The problem was solved by adding an additional layer to the film that contained a UV filter. This made the film effectively blind to the static sparks. (90% of the energy in a static spark is in the UV region of the spectrum.) The first problem was solved, but the extra layer slowed the bleaching of the film. After the dyes are formed in a color photographic film, the silver must be removed from the film. A bleaching agent oxidizes the metallic silver and a fixing agent solubilizes the silver so it can be removed from the film. The speed of these reactions is influenced by the diffusion of the bleaching agent into the film. An extra layer in the film increases the path length for the bleaching agent and slows down the silver removal.

Most color film processes use separate bleach and fix steps. Color photographic paper (which has less silver) uses a combined bleach-fix step. In an effort to simplify the process, this movie film process used a combined bleach-fix. The five component solution was known to be highly interactive.

Problem Statement

The bleach-fix does not reliably remove all of the silver in the allotted time. In the desired state, virtually all of the silver will be removed in ¾ of the allotted time.

Experiment design

At the time, I had no training in experiment design. I consulted one of the company's statistical experts. We discussed the potential factors in the experiment, our testing methods, and our capacity to run multiple experiment combinations. We chose a central composite design based on a full factorial. There was only one key response. We processed the film through the standard developers and through each one of the bleach-fix solutions for ¾ of the standard time. We analyzed the film for residual silver content. A secondary response was solution stability. How long would it last until it decomposes? This is much more difficult to test. It was also believed to be simpler to manage. To fix a drop in stability, we could simply increase the preservative.

Experiment design and results

Yates Code	Design Order	Run Order	A: Bleaching Agent	B: Fixing Agent	C: Bleach Accelerator	D: Grain Cracker	E: Preservative	Total Silver
0	43	1	0	0	0	0	0	24.2
e	17	2	-1	-1	-1	-1	1	171.1
b	3	3	-1	1	-1	-1	-1	101.6
0	44	4	0	0	0	0	0	18
+E	42	5	0	0	0	0	2.14	35.7
d	9	6	-1	-1	-1	1	-1	138.9
a	2	7	1	-1	-1	-1	-1	93.4
ace	22	8	1	-1	1	-1	1	72.4
de	25	9	-1	-1	-1	1	1	131.1
ab	4	10	1	1	-1	-1	-1	79.7
abce	24	11	1	1	1	-1	1	35.9
ad	10	12	1	-1	-1	1	-1	63.5
-C	37	13	0	0	-2.14	0	0	145.2
bcde	31	14	-1	1	1	1	1	78.2
ce	21	15	-1	-1	1	-1	1	121
-D	39	16	0	0	0	-2.14	0	53.1
c	5	17	-1	-1	1	-1	-1	102.5
-E	41	18	0	0	0	0	-2.14	2.6
abde	28	19	1	1	-1	1	1	72.3
bce	23	20	-1	1	1	-1	1	109.8
abe	20	21	1	1	-1	-1	1	89
ac	6	22	1	-1	1	-1	-1	85.3
abc	8	23	1	1	1	-1	-1	9.8

abd	12	24	1	1	-1	1	-1	72.9
acd	14	25	1	-1	1	1	-1	96.2
cd	13	26	-1	-1	1	1	-1	71
bc	7	27	-1	1	1	-1	-1	97.6
ae	18	28	1	-1	-1	-1	1	88.3
+C	39	29	0	0	2.14	0	0	100.4
ade	26	30	1	-1	-1	1	1	55.9
0	46	31	0	0	0	0	0	17.4
bd	11	32	-1	1	-1	1	-1	103.6
be	19	33	-1	1	-1	-1	1	97.2
-1	1	34	-1	-1	-1	-1	-1	157.4
cde	29	35	-1	-1	1	1	1	98.1
-B	35	36	0	-2.14	0	0	0	129.7
acde	30	37	1	-1	1	1	1	89.4
bde	27	38	-1	1	-1	1	1	87.6
abcd	16	39	1	1	1	1	-1	8.3
abcde	32	40	1	1	1	1	1	30.2
-A	33	41	-2.14	0	0	0	0	180.9
0	45	42	0	0	0	0	0	9.7
+A	34	43	2.14	0	0	0	0	85.6
+D	40	44	0	0	0	2.14	0	23.5
+B	36	45	0	2.14	0	0	0	53.6
bcd	15	46	-1	1	1	1	-1	78.3

Analysis

In those days, analysis required keying the data into a mainframe computer, running a program, and generating paper output. The first thing we learned was that the preservative had no impact on the residual silver. The other four components all had an impact and participated in interactions.

Regression Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	18.014863	4.356318	4.14	0.0002*
A: Bleaching Agent	-22.01712	1.68071	-13.10	<.0001*
B: Fixing Agent	-15.70459	1.68071	-9.34	<.0001*
C: Bleach Accelerator	-12.52436	1.68071	-7.45	<.0001*
D: Grain Cracker	-7.286669	1.68071	-4.34	0.0001*
A: Bleaching Agent*B: Fixing Agent	-0.283035	1.906124	-0.15	0.8829
A: Bleaching Agent*B: Fixing Agent*C: Bleach Accelerator	-14.11825	1.906124	-7.41	<.0001*
B: Fixing Agent*C: Bleach Accelerator	-2.887358	1.906124	-1.51	0.1393
B: Fixing Agent*C: Bleach Accelerator*D: Grain Cracker	-3.787117	1.906124	-1.99	0.0553
A: Bleaching Agent*A: Bleaching Agent	25.265965	1.833865	13.78	<.0001*
B: Fixing Agent*B: Fixing Agent	16.180005	1.833865	8.82	<.0001*

Term	Estimate	Std Error	t Ratio	Prob>|t|
C: Bleach Accelerator*C: Bleach Accelerator	22.981002	1.833865	12.53	<.0001*
D: Grain Cracker*D: Grain Cracker	4.5346648	1.833865	2.47	0.0187*

I've learned since this project that three-way interactions are quite rare. I have yet to find another DOE that contained two significant three-way interactions. The standard bleach-fix formula left 18 mg/ft^2 of silver. The prediction for an optimized formula was 2 mg/ft^2. A verification study showed that the new formula significantly improved the removal of silver from the film although the grain cracker tended to build up in solution as more film was processed. We eliminated this component so that the solution would be close to ideal after the solution was "seasoned" with film.

Formula Comparison (in design units)

Component	Original Formula	Optimized Formula
Bleaching agent	0	+0.56
Fixing agent	0	+0.70
Bleach accelerator	0	+0.49
Grain cracker	0	-2.14
Preservative	0	0
Total Silver	18 mg/ft^2	2 mg/ft^2

A side-by-side stability test showed that the new formula was close to the old formula and more than adequate.

Personal Impact

I was hooked on design experiments. There was no way I was going to achieve these results without taking interactions into account. The speed and efficiency of a factorial experiment was also evident. I signed up for the next available session of a Design of Experiments course. I'm still studying new and improved experimental designs.