Optimizations of High Energy Explosives Utilizing JMP

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Abstract

Explosives research and development is a constant balance of tradeoffs between explosive energy output and material sensitivity. One solution to optimizing a formulation for maximum performance with minimal sensitivity is energy partitioning, in which non-crystalline energetic binder materials are used to reduce the concentration of highly sensitive crystalline explosive ingredients. For this reason, a cast-cure binder system containing a novel energetic pre-polymer has been considered to replace the inert binders of legacy formulations. In order for the new ingredient to be incorporated and tested two types of statistical optimizations were performed. First, the binder components and cure chemistry were optimized through a factorial design including continuous and categorical factors. Second, a mixture design of experiments was created to determine the optimal ingredient ratios capable of meeting and out-performing a legacy cast cure explosive. Thermochemical calculations were used to populate a series of explosive performance responses in order to create models capable of predicting theoretical formulation characteristics. Both binder and formulation optimizations were analyzed using various JMP capabilities to balance trade-offs and visualize the working design space. This presentation will cover the background of cast cure explosive formulations plus the binder and explosive formulation optimizations utilizing JMP profilers.

Introduction

The Army's need for a cast cure explosive with superior performance and reduced sensitivity has never been greater. State of the art weapon designs are constantly requiring the implementation of additional electronics and longer range propulsion systems; both requirements leading to reduced space for warhead explosives. However, separate requirements also demand that the reduced volume explosives provide the same energy on target and remain insensitive to unintended stimuli such as being shot with a stray bullet or stuck in a fire[1]. These series of requirements are naturally confounding and make designing novel explosives a balancing act. Fortunately, through the use of various experimental designs, Army researchers have begun developing a very promising solution to all of these issues. Through two separate design of experiments (DoX) a cast cure explosive with enhanced performance and sensitivity measures has been realized.

The first design of experiments focused on optimizing the parameters associated with the binder system. Nearly all warhead explosives require at least two key components: a solid, crystalline explosive and a binder system to hold the crystals together forming a consolidated, highly dense explosive[2]. This binder system is traditionally polymeric in nature. In a cast cured explosive, a chemical reaction takes place within the binder system after the material is loaded into its intended casing to generate a polymeric scaffold. The most traditional cure chemistry utilized is the urethane linkage. Urethane linkages bring together an alcohol terminated pre-polymer with a multi-functional isocyanate in a covalent chemical reaction causing a liquid binder to permanently cure into a firm, rubber

consistency. Solid, crystalline ingredients such as nitramines, can be added to this liquid binder prior to the completion of the cure, creating a flow-able paste which can be loaded into any desired casing[3]. With the intention of creating a high energy, low sensitivity cast cure explosive, the pre-polymer used in this effort was an energetic material with the consistency of honey[4]. In order to turn this sticky, viscous pre-polymer into a free flowing liquid, a plasticizer was added. This small, non-reactive molecule behaves as a traditional plasticizer in the sense that it lowers the pre-polymer's viscosity and maintains a flexible rubber consistency post-cure. Additionally, like the pre-polymer, the plasticizer chosen for this effort was also an energetic material.

Despite the energetic nature of the binder ingredients, the explosive power of the resulting rubber is not sufficient for high energy applications. By incorporating crystalline nitramine powders, the explosive performance of the formulation can be increased to desirable levels. However, introducing crystalline nitramines does increase the sensitivity. Following the concept of energy partitioning, the formulation can leverage explosive energy from the binder system while the nitramine loading level is significantly reduced. This results in an insensitive, mechanically robust explosive that still delivers the desired explosive output. At this point in the development, a mixture DoX was called upon to begin modeling and predicting the trade space associated with the various formulation ingredients. Because the pre-polymer is difficult and expensive to produce, thermochemical calculations were used to create predicted performance measures about each of the mixture design combinations. Ultimately, a full understanding of the individual binder components and the mixture components was realized and used to drive the selection of formulations worthy of explosives testing.

Experimental:

Binder Factorial DoX:

In order to reduce the amount of material consumed during binder optimization experiments a full factorial design of experiments was used to guide mixture amounts. Three factors were built into the design; one categorical and two continuous. The categorical factor was the type of isocyanate where two different materials were employed. Both materials were received from Bayer Material Science and used as received. The continuous factors were the plasticizer to polymer ratio (P_l:P_o) which was varied from 1:1 to 2:1, and the isocyanate amount expressed as a ratio of isocyanate to alcohol (NCO:OH ratio) which was varied from 0.85 to 1.15 with a center point at 1.00. The resulting design space called for 12 different mixes to be created and analyzed (Figure 1, Table 1). Small scale hand mixes were blended to uniformity, degassed with a speed mixer, and analyzed for viscosity on a Malvern Kinexus Rheometer. Rheometry measurements were taken at 50^{o}C with a sheer rate ramp from zero to two hundred s^{-1} over five minutes with the minimum viscosity point being recorded as a single point response. Remaining materials were cured in a 60^{o}C oven over night. Resulting gum stocks were analyzed for hardness through use of a forced ranking system which scored their hardness numerically with respect to one another.

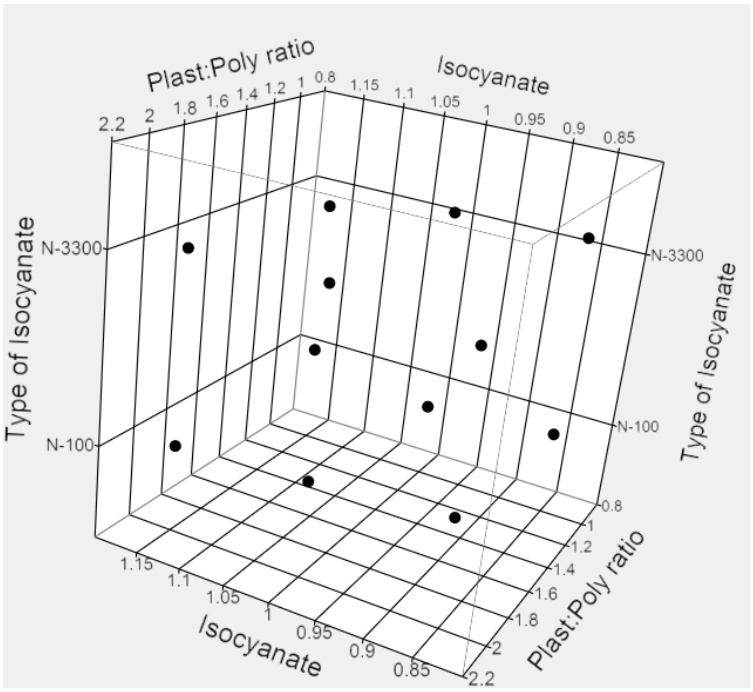


Figure 1. Factorial design of experiments for binder optimization

Formulation Mixture DoX:

A mixture design of experiments was created with JMP software so as to model the performance of the developing explosive formulation. Components of the mixture were explosive (nitramine), binder, and additive with the mixture parameters varying from 50-90%, 10-50% and 0-30% weight respectively. Second order interactions and a center point were built into the design resulting in a 12 run DOE (Figure 2). These 12 theoretical formulations were input into a thermochemical code. The responses acquired for each formulation included the density, pressure, temperature, shock, expansion, and energy (Table 2). Least squares regression analysis was employed to create models of the response data. Three verification formulations (Table 3) were also created, run in the code, and compared to the model predicted values to test model validity.

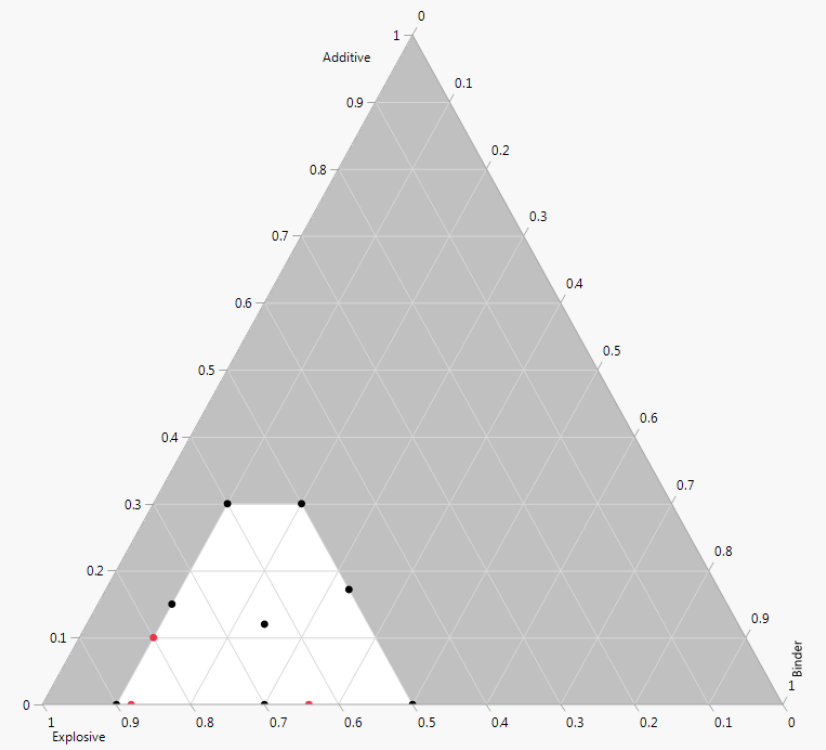


Figure 2. Ternary plot of the mixture design space with black points indicating the initial design points and red points indicating verification runs.

Results:

Binder Results:

Table 1. Minimum viscosity and forced ranking hardness values

Isocyanate Level	Pl:Po	Type of Isocyanate	Viscosity (Pa*s)	Hardness Score
1.00	2	N-3300	0.04138	18
1.00	2	N-100	0.04632	8
1.15	2	N-3300	0.04263	26
1.15	1	N-3300	0.13540	70
0.85	2	N-100	0.04420	1
1.00	1	N-3300	0.13030	52
1.00	1	N-100	0.12870	53
0.85	2	N-3300	0.04251	1
1.15	1	N-100	0.13170	67
0.85	1	N-100	0.13790	40
1.15	2	N-100	0.04354	26
0.85	1	N-3300	0.13320	40

Formulation Results:

Table 2. Thermochemical calculation response data on each mixture DOE run (normalized).

Run #	Density	Pressure	Temperature	Shock	Expansion	Energy
1	0.788961	0.6853	0.6486	0.859	-1.00	-1.000
2	0.895428	0.7664	0.7661	0.891	-1.33	-1.4693
3	0.847407	0.7897	0.6533	0.923	-1.16	-1.1372
4	1.00000	0.6902	1.000	0.842	-1.23	-2.5771
5	0.877749	0.6670	0.8068	0.835	-1.25	-1.529
6	0.788961	0.6853	0.6486	0.859	-1.00	-1.000
7	0.958121	0.6107	0.9735	0.801	-1.13	-2.4434
8	0.915201	1.000	0.6531	1.00	-1.37	-1.3025
9	0.955723	0.8743	0.8288	0.933	-1.49	-1.6973
10	0.915201	1.000	0.6531	1.00	-1.37	-1.3025
11	0.847407	0.7897	0.6533	0.923	-1.16	-1.1372
12	1.00000	0.6902	1.000	0.842	-1.23	-2.5771

Table 3. Thermochemical calculation response data compared to prediction model responses from design of experiments for verification formulations (normalized).

Verification Run #	Density	Pressure	Temperature	Shock	Expansion	Energy
1 Calc	0.9079	0.9752	0.6539	0.992	-1.34	-1.2845
1 Model Prediction	0.9079	0.9742	0.6545	0.992	-1.34	-1.2868
2 Calc	0.8290	0.7409	0.6505	0.902	-1.11	-1.0934
2 Model Prediction	0.8289	0.7455	0.6506	0.902	-1.11	-1.0957
3 Calc	0.9418	0.9204	0.7761	0.956	-1.47	-1.5582
3 Model Predition	0.9419	0.9218	0.7696	0.958	-1.48	-1.5329

Table 4: Small scale sensitivity test results.

Formulation	ERL Impact (cm)	BAM Friction (N)
56% nitramine	>100	>360
88% nitramine	42.2	324
RDX CL 1	24.2	160
Legacy Baseline	32	n/a

Discussion:

An optimized binder system containing an energetic pre-polymer, an energetic plasticizer, and an isocyanate was constructed through the use of a full factorial design of experiments. This particular design was chosen for the types of factors and responses available with this material. Because the isocyanate content is a calculated ratio relative to the amount of polymer used, it was not possible to use a mixture DoX. A fractional factorial DoX would have resulted in a reduced number of runs, but would have confounded the main effects observed in the responses. By executing a full factorial design, all main affects were able to be realized in a linear manner. If the responses of hardness and viscosity are, in fact, non-linearly correlated with the factors, further experimentation is necessary to resolve the curvature. The values for each factor were guided by previous formulation values. Factors were selected based on prior experience with similar types of cast cure binders: the plasticizer to polymer ratio (P_l:P_o), the amount of isocyanate, and the type of isocyanate. The P_l:P_o is the most important factor among these three. If the ratio is too low, the viscosity of the mix will be too high and the resulting rubber will be too brittle. If the ratio is too high, the rubber will lack mechanical integrity and there is a risk that excess plasticizer may exude over time. The amount of isocyanate is also key as an under-cured binder with too little isocyanate will never reach a rubbery state. However, an over-cured binder can become brittle or the excess isocyanate can react with other species to produce detrimental byproducts. The two types of isocyanates considered in this effort differed very little with respect to chemistry, but had different viscosities, potentially affecting the final mix viscosities.

Selection of the optimal binder constituents was achieved through a least squares regression analysis of the resulting data followed by a trade-off analysis aimed at determining a firm product (hardness) with minimal viscosity to aid in processing the final formulation. First, the minimum hardness score was chosen to be 55 based on the observations of the mechanical integrity of the resulting gum stocks. Anything softer would result in a mechanically weak formulation. With that response constrained, maximization of the hardness was most easily achieved by setting the isocyanate level to 1.15 because the amount of isocyanate only affected the hardness and had no effect on the viscosity. This setting was limited to 1.15 so as to avoid previously mentioned detrimental effects of excess isocyanate despite the model's indication that additional isocyanate would lead to a stronger rubber. Holding the hardness value constant at the minimum 55, and the isocyanate level at 1.15, other factors were dialed in order to minimize the viscosity. As demonstrated by the JMP profiler (Figure 3) the isocyanate type had little effect on the viscosity, but the effect of P_l:P_o was significant. Consequently, N-3300 was chosen for ease of processing with little effect on the formulation and a P_l:P_o of 1.33; the maximum P_l:P_o that could be used without lowering the hardness below 55.

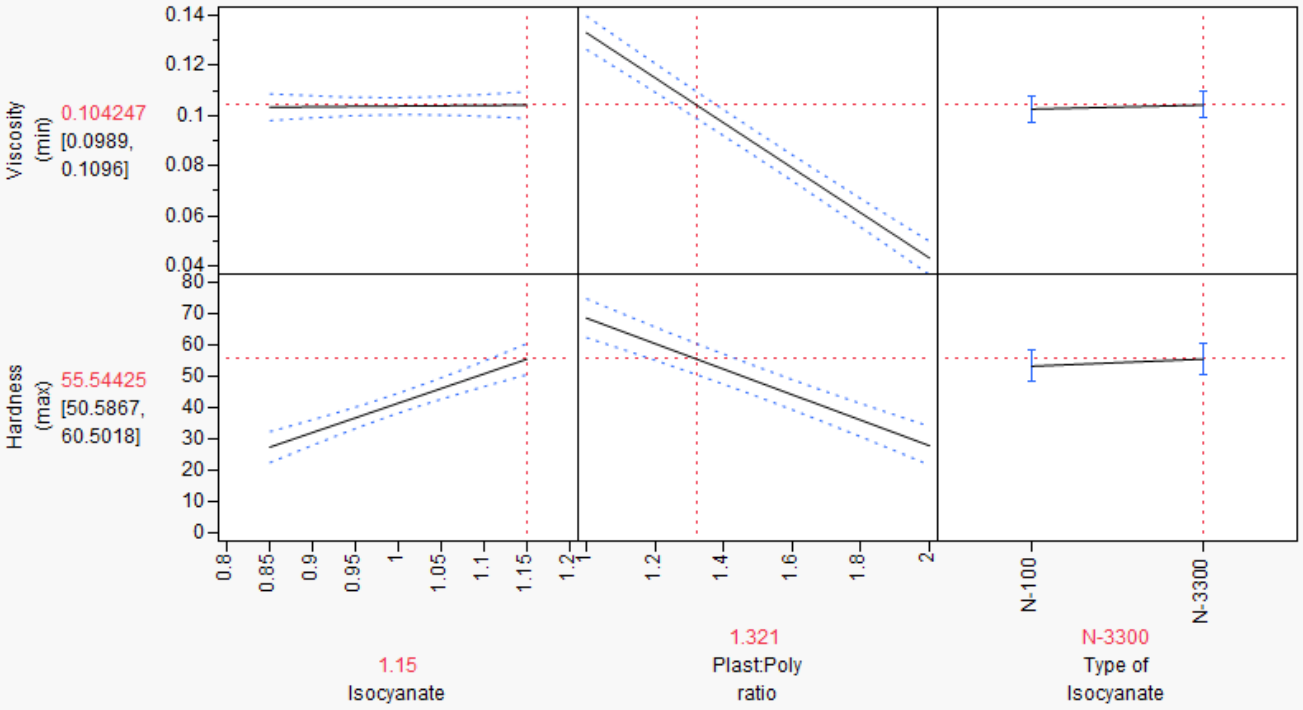


Figure 3. JMP Profiler modeling the responses of hardness and viscosity against all three factors in the binder optimization DoX.

Optimization of the solid nitramine content in the formulation was performed through a combination of a mixture DoX and thermochemical calculations. Calculated performances were used to populate the responses for each of the theoretical DoX formulations. Least squares regression analysis applied to those responses resulted in best fit equations capable of predicting the performance of any formulation created within the design space. Only statistically relevant factors were considered in the creation of each of the respective models. Three formulations that varied in composition from the DoX runs were created and used to verify the models. A comparison of the model responses and the thermochemically calculated responses can be found in Table 3. It was immediately evident that all response models were extremely accurate. Predictions vary from the thermochemical calculations with less than 2% error, thus validating the models. As the primary goal of this project was to create a formulation whose performance and sensitivity were superior to legacy explosives, the calculated responses for a legacy baseline containing 88% nitramine were used to establish bounds within the design space. The overlay of the prediction models and the subsequently established bounds on the ternary plot of the design space can be seen in Figure 4. The various color schemes correspond to the different responses. Any unshaded region within the design space represented a possible formulation combination that would exceed the baseline.

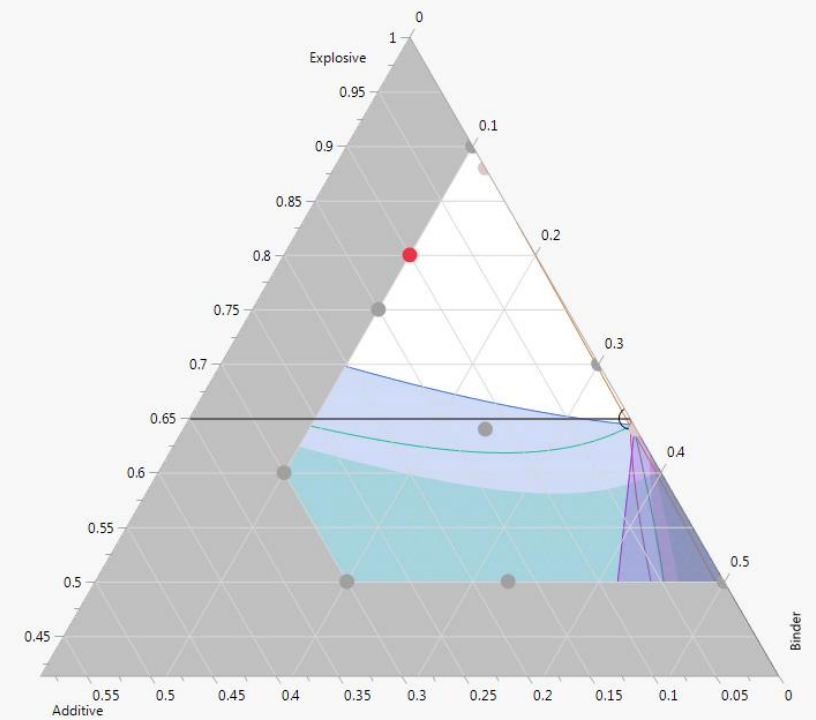
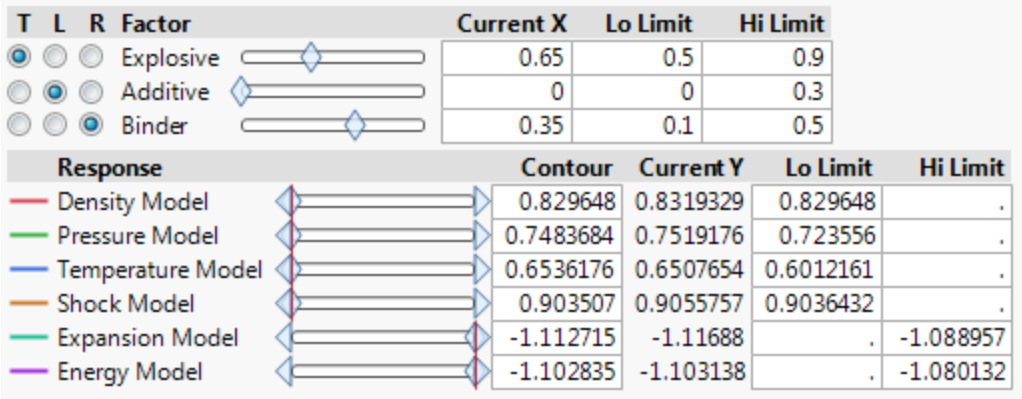


Figure 4. Ternary plot of the mixture design space with overlaid response models and bounds establishing baseline performance metrics.

A different mixture profiler directly showed the effects of altering the ingredient amounts within the confines of the mixture; i.e. always summing to one. Any formulation within the design space could be created and have all of its performance metrics predicted simultaneously. By altering the formulation values in the profiler to match the bounds of the baseline metrics, an initial target formulation was deduced. Figure 5 shows that every performance measure for the baseline can be met or exceeded with a formulation that contains 65% nitramine explosive and 35% binder. With the intention of bookending the performance limits of this design space, that formulation and a formulation with 88% nitramine explosive were considered for future testing. This will provide a direct “drop in” replacement binder formulation as well as an iso-energetic formulation to compare to the baseline. Inclusion of the “additive” has been eliminated from the earliest formulation attempts in order to confidently attribute all energy and sensitivity measures to the inclusion of the energetic pre-polymer in the binder system.



T	L	R	Factor	Current X	Lo Limit	Hi Limit
◉	○	○	Explosive	0.65	0.5	0.9
○	◉	○	Additive	0	0	0.3
○	○	◉	Binder	0.35	0.1	0.5

Response	Contour	Current Y	Lo Limit	Hi Limit
Density Model	0.829648	0.8319329	0.829648	.
Pressure Model	0.7483684	0.7519176	0.723556	.
Temperature Model	0.6536176	0.6507654	0.6012161	.
Shock Model	0.903507	0.9055757	0.9036432	.
Expansion Model	-1.112715	-1.11688	.	-1.088957
Energy Model	-1.102835	-1.103138	.	-1.080132

Figure 5. JMP mixture profiler with target formulation identified against the legacy baseline formulation.

Preliminary formulations were mixed on the small scale according to both bookends of the design space and the results can be found in Table 4. Both formulations exhibited superior sensitivity to a Class 1 RDX standard. However, the most important comparison is between the two bookend formulations. The test results indicated that despite the iso-energetic performance calculations, the sensitivity of the 65% nitramine formulation is superior to the baseline legacy explosive. Test fixtures for various experimentally determined explosive performance and sensitivity measurements are planned for the near future. Performance test results will verify the thermochemical calculations as well as the model predictions. Sensitivity tests of these formulations and others containing similar ingredients will begin to establish an empirical model capable of predicting the sensitivity trade-space specific to these materials. Additional formulations containing the additive will then be pursued to fully realize the entire potential of the formulation design space.

Summary and Conclusions

A cast cure binder system containing a novel energetic pre-polymer was created through a factorial design of experiments. Hardness and viscosity of the neat binder system were optimized through a trade-off analysis with a JMP profiler. Thermochemical calculations of performance for formulations containing the new binder were used to populate responses for a mixture DoX resulting in two book end formulations to be targeted for testing. The low bookend formulation meets legacy formulation performance measures with only 65% nitramine and the high bookend provides a direct binder replacement comparison with 88% nitramine. Initial results indicate that performance of the new formulations will be superior to that of the baseline while simultaneously exhibiting improved sensitivity.

References:

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