Reduction of Ostwald Ripening with Low-cost Surface Treatment of Basic Copper Nitrate

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Abstract

The morphology and surface area of basic copper nitrate (BCN) can be retained over time with the use of surface modification additives. In this work, we show how a known failure mode of generant materials can be mitigated with a simple and highly-effective additive treatment. BCN accounts for about 50% of the composition of the most widely-used pyrotechnic generant formulation. Failures in ammonium nitrate generant airbag modules have been linked to Ostwald ripening of the generant particles.[1,2] Addition of a small amount of commonly available additives to BCN is sufficient to drastically decrease the loss of surface area seen with Ostwald ripening.[3] We report our results testing sorbitol, glycerol, dextrose, triethanolamine, and alkanolamines (THEED and THPED). The additives were tested at levels of 0.1 – 1.0% at several temperatures (8 – 85° C) and partial pressures of water vapor (5 – 95% relative humidity) for five days. Sorbitol was most effective, showing no measurable relative surface area loss even under the harshest conditions. Sucrose was similarly effective showing <4% relative surface area loss under the same conditions. The ballistics properties of generant formulated with surface coated BCN were not significantly affected. These simple and cost-effective surface treatments may offer an opportunity to protect BCN from Ostwald ripening in generant formulations.

Introduction

Automobile airbags have saved hundreds of thousands of lives since their widespread adoption in highway vehicles in the 1980s. While the successes of airbags have certainly been a great benefit to society, no technology is perfect. Some well-known failures of airbags have caused problems and the industry has responded by identifying root causes and making improvements. An example of this is the incidents with ammonium nitrate fueled airbags that came to light in the 2010s. The root cause analysis contracted by the NHTSA found that Ostwald ripening of the generant to be the most likely origin of these failures.

BCN makes up a significant fraction of the generant in several airbag designs. Like all solids, BCN is susceptible to Ostwald ripening. We reasoned that if this process had a negative impact in the behavior of other generant materials, we should understand what it does to BCN. We set out to study the extent to which this occurs and if and how it can be reduced. In previous, unpublished work, we learned that addition of a small amount of sugar or other small, hydroxyl-functionalized additive could slow or eliminate oxidation and loss of surface area in other solid particles. In 2018, we reported initial success with this approach in reducing the impact of age on the loss of surface area in BCN.

Since then, we have expanded our testing, disclosed our additives, and decreased the loadings to find how effective this coating can be before breaking down due to time or insufficient coverage. Figure 1 shows the molecular structures of the compounds tested as surface coatings in this work.

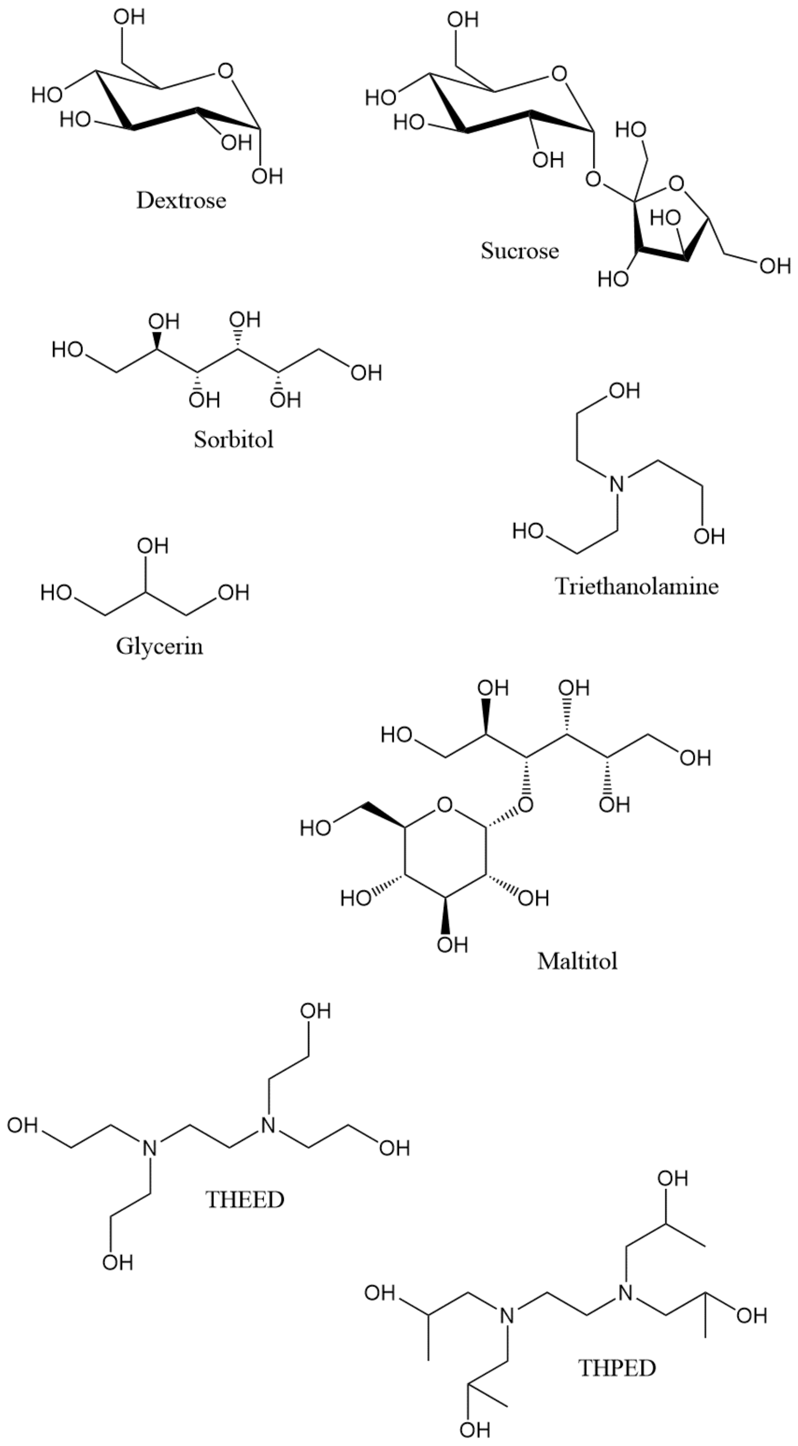

Figure 1. Molecular structures of the candidate coating for BCN. THEED is tetrahydroxyethylethylenediamine, and THPED is tetrahydroxypropylethylenediamine.

Experimental

Sample Preparation

Standard grade BCN was produced by a proprietary process at the Shepherd Chemical Company, Norwood, OH, USA.

To 50 lb of BCN slurried in 117 lb water was added an appropriate amount of additive to achieve the target level. The resulting slurry was spray dried with an outlet temperature sufficient to achieve <0.2% residual moisture as measured by thermogravimetric analysis to constant mass at 105 °C.

Sample Accelerated Ageing

Samples were subjected to conditions of accelerated ageing in a CSZ test chamber model ZPH-8-2-H/AC for 5 days, unless otherwise indicated. Temperature control is ± 0.5 °C and relative humidity control is ± 2%.

Surface Area Determination

For BET measurements samples were degassed using a Micromeritics SmartPrep degasser and subsequent analysis was conducted using a Micromeritics Tristar 3020 surface analyzer. The relative standard deviation of the tests in this study is approximately 0.15 m^2/g.

Results and Discussion

We have previously reported on the effects of ageing on the diffraction patterns, particle size distributions, microstructures, moisture content, and densities. Ageing had minimal effect on these properties, so we will not discuss them further now.[4] In that study we also reported that heat and temperature had a large effect on the specific surface area (SSA) of untreated BCN, losing more than half its initially measured value under similar test conditions to those reported here.

Table 1 and Figure 2 show the collected results of the SSA changes after accelerated ageing.

Condition		8° C, 5% RH	8° C, 95% RH	25° C, 25% RH	50° C, 50% RH	65° C, 75% RH	65° C 95% RH	85° C, 5% RH	85° C, 75% RH	85° C, 95% RH
Amount and Additive	Original SSA (m^2/g)									
0.1% Dextrose	4.98	-0.20	-0.25	-0.23	-0.24	-0.21	-0.36	-0.39	-0.47	-0.20
0.1% Glycerin	4.26	-0.13	-0.09	-0.09	-0.31	-0.31	-0.10	-0.23	-0.39	-0.37
0.1% Sorbitol	4.86	0.00	0.12	0.13	0.08	0.01	0.08	-0.08	-0.26	0.00
0.1% Sucrose	4.87	-0.02	0.05	-0.23	-0.05	-0.23	-0.07	-0.09	-0.34	-0.05
0.25% Dextrose	5.10	0.28	0.45	0.31	0.29	0.07	0.22	0.34	0.07	-0.18
0.25% Sorbitol	5.28	-0.09	-0.08	-0.03	-0.05	0.11	-0.31	-0.08	-0.16	-0.36
0.25% Sucrose	5.14	0.05	-0.02	0.07	-0.01	-0.07	-0.09	0.00	-0.05	-0.23
0.5% Dextrose	4.96	0.10	0.07	0.00	0.05	-0.01	-0.23	-0.06	0.05	0.11
0.5% Sorbitol	4.61	0.08	0.09	0.21	0.10	0.22	0.08	0.01	0.31	0.31
0.5% Sucrose	4.79	-0.08	-0.16	-0.23	-0.08	0.04	0.03	0.20	0.05	0.06
1% Dextrose	4.91	0.07	0.03	0.12	0.00	0.12	0.25	0.00	0.36	0.46
1% Glycerin	4.85	-0.10	-0.19	-0.17	-0.37	-0.47	-0.57	-0.17	-1.02	-0.73
1% Maltitol	4.55	0.03	0.01	-0.03	-0.47	-0.47	-0.29	-0.14	-0.15	0.23
1% Sorbitol	4.43	-0.18	-0.06	0.10	0.00	0.13	0.12	0.00	0.37	0.44
1% Sucrose	4.45	-0.06	0.04	0.08	-0.17	0.00	0.12	0.07	0.34	0.21
1% TEA	4.61	-0.24	0.04	-0.06	-0.06	-0.29	-0.16	0.01	-0.32	-0.24

Table 1. Changes in SSA observed for BCN under accelerated ageing with various conditions. The shaded values are reductions of the SSA that are outside of the estimated relative standard deviation.

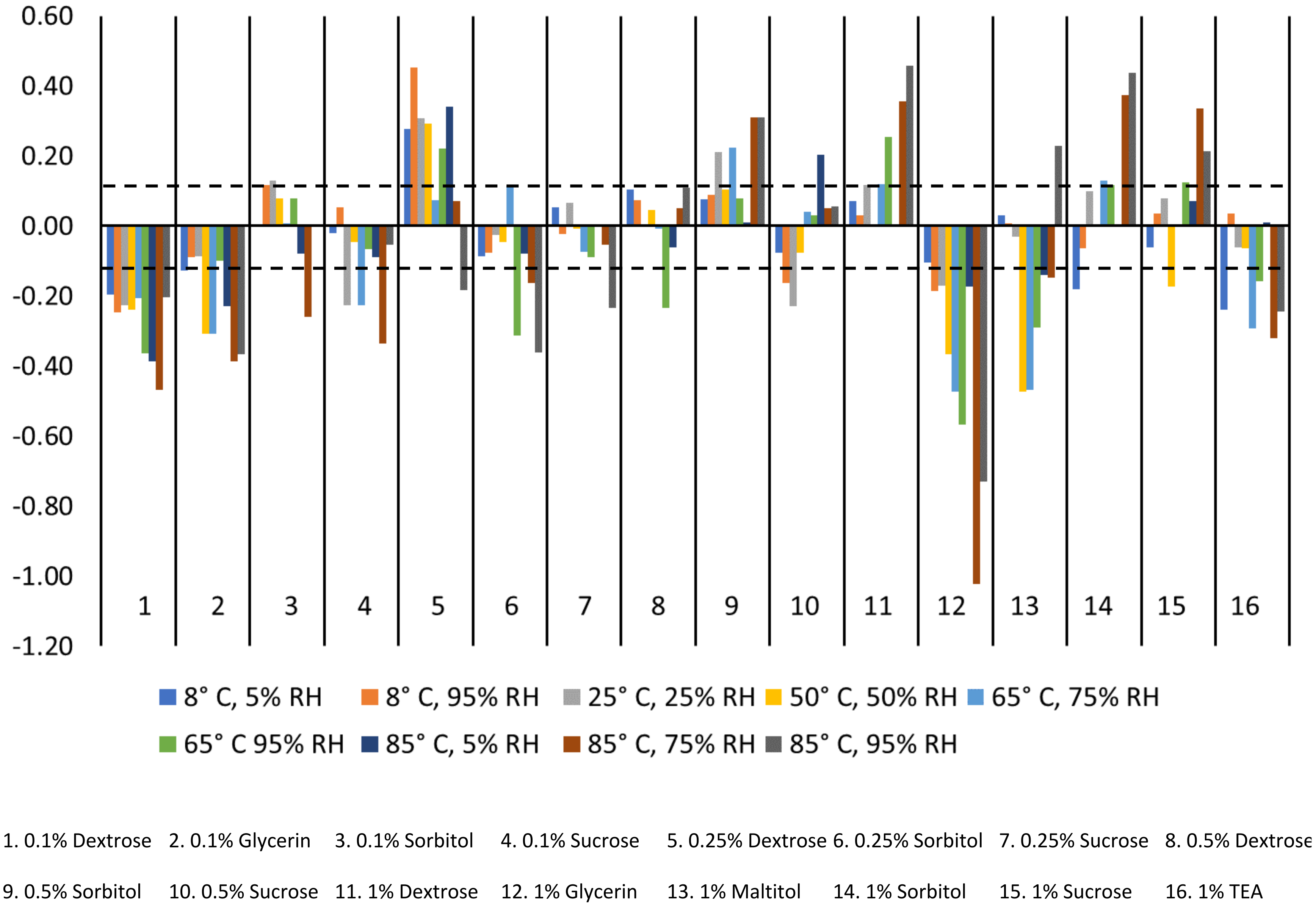
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
-1.20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
8° C, 5% RH
8° C, 95% RH
25° C, 25% RH
50° C, 50% RH
65° C, 75% RH
65° C 95% RH
85° C, 5% RH
85° C, 75% RH
85° C, 95% RH
1. 0.1% Dextrose
2. 0.1% Glycerin
3. 0.1% Sorbitol
4. 0.1% Sucrose
5. 0.25% Dextrose
6. 0.25% Sorbitol
7. 0.25% Sucrose
8. 0.5% Dextrose
9. 0.5% Sorbitol
10. 0.5% Sucrose
11. 1% Dextrose
12. 1% Glycerin
13. 1% Maltitol
14. 1% Sorbitol
15. 1% Sucrose
16. 1% TEA

Figure 2. Specific surface area changes from Table 1 in m^2/g. The dashed lines show the level of the estimated relative standard deviation.

Dextrose

Dextrose coated material lost some surface area during the 5-day tests. But the BCN still maintained over 90% of its original surface area under all the conditions. It can be seen in Table 1 that compared to the other additives, dextrose was not the most effective at preventing surface area loss. Two of the dextrose treated samples, 0.25 and 1%, showed increases in SSA that are probably significant. We speculate that clustering of the dextrose into droplets may have formed pockets in the surface, leading to the observed increase. This behavior is only seen with the sugar additives, leading us to believe that some common mechanism for this result is probably at play. Additional study would be required to further investigate these observations.

Glycerin

At a low additive rate, glycerin was one of the more effective additives. But upon increasing the addition rate, the performance dropped and was actually the least effective additive of those that were studied thoroughly. The samples lost over 10% of their surface area, on average, with the sample held under the harshest conditions losing over 20%. It may be that the hydrophilic interaction with the surface is overwhelmed by intermolecular interactions, forming hydrophilic channels to the surface that water molecules can traverse.

Sucrose

Under all conditions, the sucrose treated samples showed very little change. Since sucrose is also a relatively inexpensive and readily available material, a sample of the 0.1% coated sample was kept in our warehouse in Norwood, OH, USA for 13 mo., during which time the conditions often reached >50% RH and >30 °C. No significant change in the SSA was measured.

Sorbitol

The sorbitol treated samples also showed relatively small changes in SSA. The sample that changed the most increased by <8% relative to the initial value. The 0.1% treated sample was kept for 18 mo. in the warehouse and no significant change to the SSA was measured.

Triethanolamine (TEA)

Triethanolamine was only tested at the 1% level but was similarly effective to some of the other additives.

Maltitol

Maltitol was tested at the 1% level and was not as effective as some of the other additives. Maltitol is also relatively expensive.

THEED and THPED

Both THEED and THPED were tested at the 1% level and the samples lost over 10% of their SSA. Considering also the relatively high cost and specialized nature of these materials, further testing was not pursued.

Burnrate Testing

A sample of 0.1% Sucrose coated BCN was provided to an airbag manufacturer. As shown in Figure 3, standard burnrate testing did not show significant differences in behavior from untreated BCN.[5]

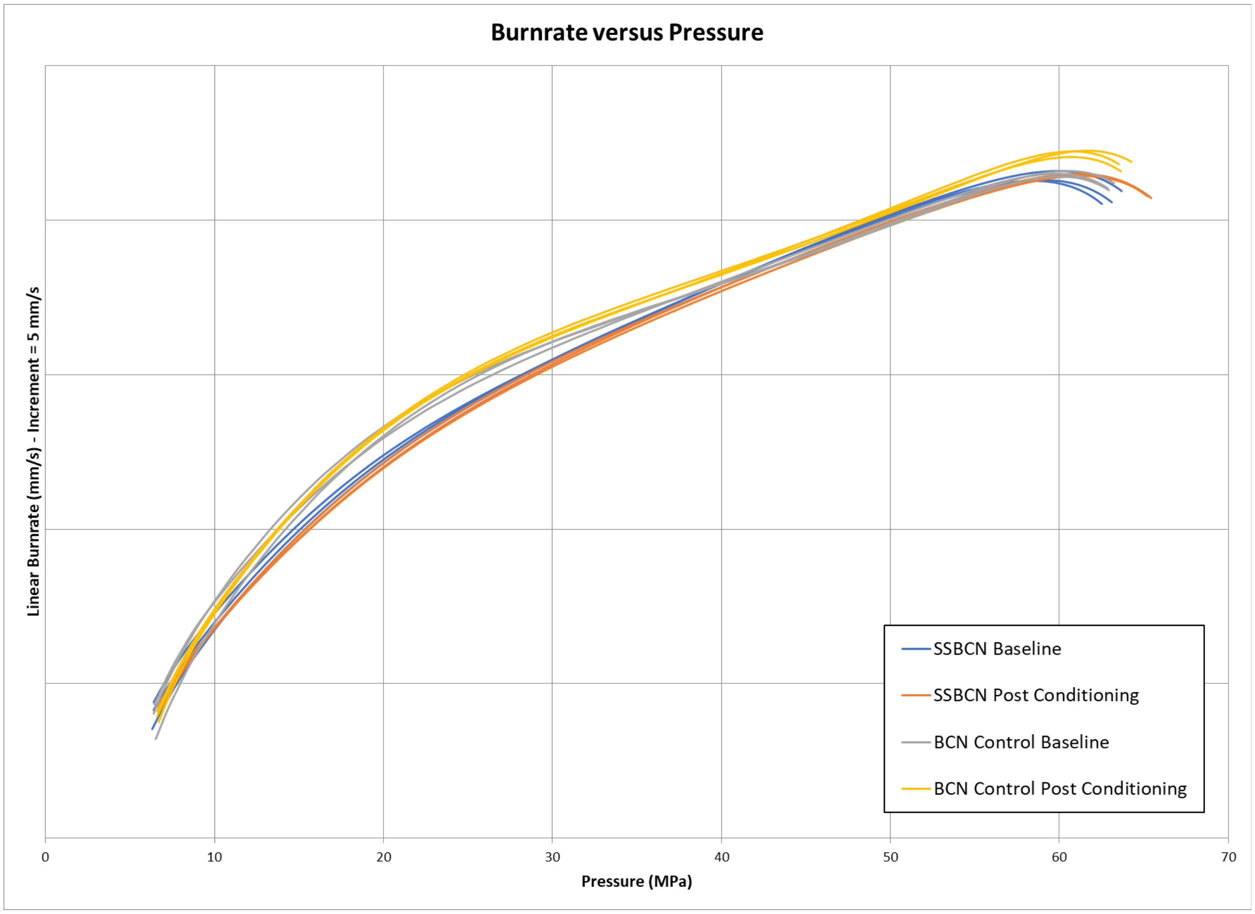

Figure 3. Burnrate testing results of 0.1% sucrose treated BCN (SSBCN) vs. untreated BCN.

Conclusions

Low level treatment of BCN with commonly available molecular materials leads to changes of surface area history under conditions of accelerated ageing and over one year of long-term storage. Treatment with, for instance, 0.1% sucrose is sufficient to maintain the surface area of BCN under long storage or aggressive accelerated ageing conditions. The presence of water, particularly at high temperatures, leads to rapid reduction of the SSA of BCN. This is almost certainly driven by surface energy reduction corresponding to increased radii of curvature of the microfeatures at the surface — the same mechanism that drives Ostwald ripening. It may be that the hydrophilic "sides" of the effective treatment molecules preferentially absorb to the BCN nitrated- and hydroxylated-surface and present a hydrophobic surface to the environment that prevents attack by water.

References

1. Orbital ATK for National Highway Transportation Safety Administration. (2016). Takata Inflator Rupture Root Cause Summary Report. https://tinyurl.com/y2frevnv

2. Schubert, B. 2018, "LESSONS LEARNED FROM INFLATOR FIELD ISSUES", Airbag2018: 14th International Symposium and Accompanying Exhibition on Sophisticated Car Occupant Safety Systems, Congress Center "Rosengarten", Mannheim, Germany, 26-28 November.

3. Harrison, R; Taylor, S. D.; and Schoster, W. E. (2021). Surface Modifiers for Preparing Age-resistant Inorganic Salts (US 20210340020A1). US Patent and Trademark Office. https://tinyurl.com/yckupr2x

4. Taylor, S. D., Huff, C., Harrison, R., Joy, T., Hart, R., Ramminger, G. 2018, "Environmental Ageing of Basic Copper Nitrate", *Airbag2018: 14th International Symposium and Accompanying Exhibition on Sophisticated Car Occupant Safety Systems*, Congress Center "Rosengarten", Mannheim, Germany, 26-28 November.

5. Personal communication, airbag manufacturing engineer, September 2022.