Supplementary Information (SI) for Environmental Science: Advances.

Performance of Hydrophilic Polyols in the Formation of Polyurethane Based Controlled Release Fertilizer Coatings

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SUPPORTING INFORMATION

Rotating Drum Coater

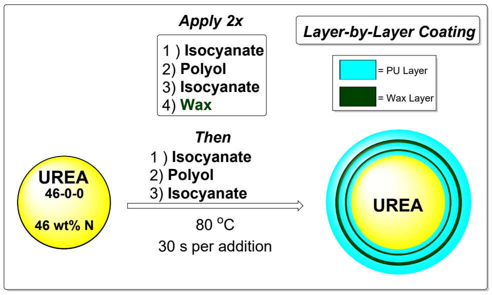
Figure S1. The rotating coater is of steel construction with a drum diameter of 16 1/8” with five (5) evenly spaced 1” baffles, an electric motor, and an angle of repose of approximately 60° from the hood surface.

Coating Procedure. Urea prills (0.5-2.0 kg) were kept in an oven set to 80 °C for up to 24 h prior to coating experiments. Using gloves for hot material handling, the prills were transferred from the oven to the coater and rotation was subsequently initiated at ca. 40 rpm. A heat gun was used to heat and maintain the temperature of the rotating prills at 80 °C, and an IR temperature probe was utilized to ensure temperature stability. Once the temperature was stabilized at 80 °C, addition of the coating was initiated. Generally, for each formulation unless otherwise noted, the following order of addition and timing was observed:

Table S1. Order and timing of additions

Isocyanate (0.4)	0 s
Polyol	30 s
Isocyanate (0.6)	60 s
Wax (50% of total)	90 s
Repeat 2 x	**30 s between additions**
Isocyanate (0.4)	240 s
Polyol	270 s
Isocyanate (0.6)	300 s

All components were pre-weighed and triethanolamine (10 wt%) catalyst was added to the polyol portion prior to addition. Following application of the final layer, the coated prills were allowed to cool to 50 °C before they were removed from the coater and set aside at room temperature for a minimum of 1 week, to allow for a full cure, after which release profile measurements could be collected.



Scheme S1. General schematic of layer-by-layer urea coating process

Refractive Index (RI) Calibration. As light travels through a transparent material, or solution, its velocity is altered and can be measured. Solvated materials influence that RI value. Using these principles, a calibration curve was generated by measuring the RI, using a Reichert AR 200 refractometer, of aqueous urea (46-0-0) solutions with varied concentrations (*See Supporting Information*). The equation can be rearranged to solve for dissolved urea in wt% as such:

Where, **X** = wt% Released Urea; **Y** = Refractive Index (RI)

$$X = \frac{Y - 1.3330}{0.0013}$$

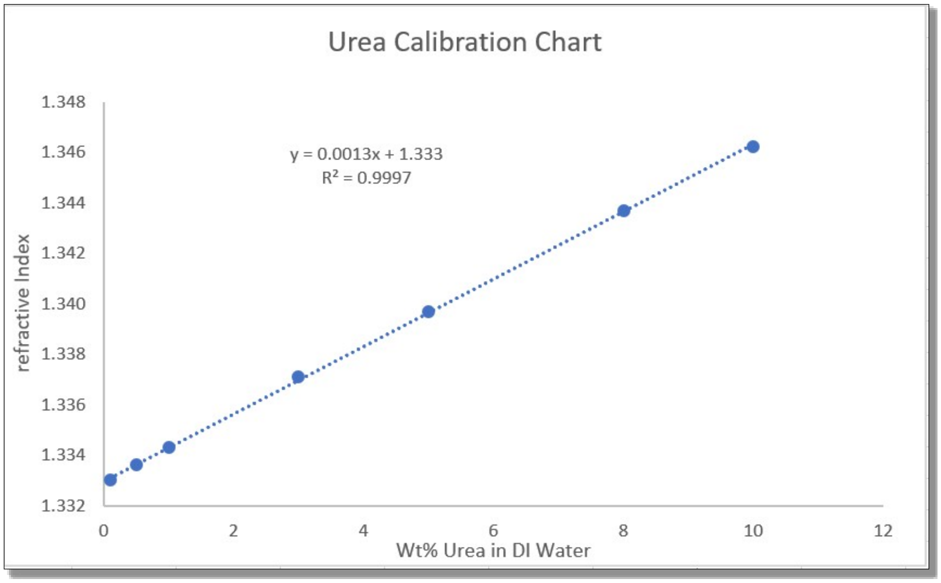


Figure S2. Refractive index calibration to measure amount of release urea in DI water

Analysis of Urea Release Performance. After a minimum of 7 days post-coating, the urea release profiles were measured by taking 10g of coated material and placing it in a jar with 100 mL of DI H_2O and kept at room temperature. The refractive index of a small aliquot was collected after 14, 28, 56, and 84 days, or until >95% urea release was measured.

Table S2. Component amounts for the formulated coatings for 1kg batch of urea (46-0-0).

	Coating Formulation Code							
Component	**A**	**B**	**C**	**D1**	**D2**	**E**	**F**	**G**
P700	11.66g					6.41 g		
Glycerol		3.65g				1.60 g	1.66 g	1.82 g
PEG-400			10.93 g				5.90 g	
TRI-625				11.18g	12.42 g			5.47 g
Triethanolamine	1.30 g	0.41 g	1.22 g	1.24 g	1.38 g	0.89	0.84 g	0.81 g
PAPI™ 27 pMDI	14.04 g	22.94 g	14.85 g	14.58 g	16.20 g	18.10 g	18.60 g	18.90 g
C_{30+HA} Wax	5.0 g	5.0 g	5.0 g	5.0 g		5.0 g	5.0 g	5.0 g
PU wt%	2.7%	2.7%	2.7%	2.7%	3.0%	2.7%	2.7%	2.7%
Wax wt%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
Total Coating wt%	3.2%	3.2%	3.2%	3.2%	3.5%	3.2%	3.2%	3.2%

Crosslink Density Calculations:

Crosslink density was normalized to elastically equivalent tetra-functional crosslinks (ie: 2 trifunctional crosslinks that become linked are elastically equivalent to 1 tetra-functional cross-link).

X = crosslink density (mmol/g); **$M_{>2Fn}$** = Mass of component with greater than 2 functionality

$EW_{>2Fn}$ = Equivalent weight of component with greater than 2 functionality

$Fn_{>2Fn}$ = Average functionality of component with greater than 2 functionality

M_{tot} = Total mass of formulation.

$$X = \frac{\sum\left[\frac{M_{>2Fn}}{EW_{>2Fn}} * \left(\frac{Fn_{>2Fn}}{2} - 1\right)\right]}{M_{tot}}$$

For example, the equivalent weight and presumed nominal functionality of each component is shown in **Table S3** reported assumptions were used to calculate the theoretical crosslink density of each formulation.

Table S3. Functionality and equivalent weight of components used in this study. Equivalent weight is determined as 56100/OH#, where the Hydroxyl number (OH#) is measured by ASTM D4274. The Isocyanate equivalent weight is determined by isocyanate content as measured by D5155. Functionality is assumed to be as reported by the supplier.

Component	Functionality (F_N)	Equivalent Weight (EW)
P700	3.0	236 g/mol
Glycerol	3	30.7 g/mol
PEG-400	2	200 g/mol
TRI-625	3	209 g/mol
Triethanolamine	3	50 g/mol

PAPI™ 27 pMDI	2.7	134 g/mol

Example Calculation: Formulation A

P700: Mass = 11.66 g; Equivalent Weight = 236 g/mol

Triethanolamine: Mass = 1.30 g; Equivalent Weight = 50 g/mol

PAPI™ 27 pMDI: Mass = 14.04 g; Equivalent Weight = 134 g/mol

$X= \{\sum([(11.66g/236\ g*mol^{-1})*(1.5 - 1)] + [(1.30g/50g*mol^{-1})*(1.5-1)] + [(14.04g/134\ g*mol^{-1})*(1.35-1)]\}/ 27\ g$ total

$X = (0.0247\ mol + 0.0130\ mol + 0.0376\ mol)/27g \rightarrow X = 0.00275\ mol/ 30g \rightarrow X = 0.00275\ mol/g$

Crosslink Density $_{\text{(Formulation A)}}$ = 2.75 mmol/g

Table S4. General compositions and controlled release performance of coating formulations. All coatings performed at 2.7 wt% polyurethane. **Coating D2** performed at 3.0 wt% polyurethane. All coatings performed with 0.5 wt% wax additive.

Coating	**Polyol 1**	**Polyol 2**	**Catalyst**	**Iso**	**14 d**	**28 d**	**56 d**
A	P700	--	TEOA	PAPI 27	24%	49%	76%
B	Glycerol	--	TEOA	PAPI 27	>95%	--	--
C	PEG-400	--	TEOA	PAPI 27	70%	>95%	--
D1	TRI-625	--	TEOA	PAPI 27	30%	64%	>95%
D2	TRI-625	--	TEOA	PAPI 27	20%	38%	90%
E	P700	Glycerol	TEOA	PAPI 27	30%	54%	71%
F	PEG-400	Glycerol	TEOA	PAPI 27	15%	31%	73%
G	TRI-625	Glycerol	TEOA	PAPI 27	10%	34%	75%

Table S5. Properties of polyols used in the study and their blends. For ease of scaling, ratios are presented for the amount of isocyanate and polyol need to achieved index 140.

						10 wt% TEOA			
Coating	**Polyol 1**	**Polyol 2**	**OH#**	**HEW**		Blend OH#	Blend HEW	%Iso	%Polyol
A	P700	--	238	236		329	171	52%	48%
B	Glycerol	--	1827	30.7		1757	32	85%	15%
C	PEG-400	--	281	200		365	154	55%	45%
D1	TRI-625	--	269	209		355	158	54%	46%
D2	TRI-625	--	269	209		355	158	54%	46%
E	P700	Glycerol	556	101		612	92	67%	33%
F	PEG-400	Glycerol	621	90		674	83	69%	31%
G	TRI-625	Glycerol	659	85		705	80	70%	30%

Griffin's Method Determination of Theoretical Hydrophilic/Lipophilic Balance

REFERENCE: *Griffin, W. C. Journal of the Society of Cosmetic Chemists.* **1949**, *1, 311–26.*

To further support the claim of hydrophilicity in the studied blends, an application of Griffin's method for the determination of hydrophilic/lipophilic balance can be readily utilized as follows:

Griffin's Method: HLB = 20*(M_h/M)

Where: M_h = Molecular Weight of hydrophilic portion; M = total Molecular Weight

If: HLB <10, then lipid soluble

If: HLB > 10, then water-soluble

Example Calculation for **Coating A**

P700 polyol is a glycerol initiated poly(propylene oxide) triol. Glycerol molecular weight is 92 g/mol, and constitutes the hydrophilic portion of the 700 MW total triol. Therefore the calculation is as follows:

(92/700)*20 = 2.62 HLB value for P700

The isocyanate-reactive blend contains 10 wt% of entirely water-soluble, hydrophilic triethanolamine (TEOA), therefore the value for TEOA is as follows:

(150/150)*20 = 20 HLB value for TEOA.

If one applies a slight modification of the HLB calculation for illustrative purposes, then the average HLB of the isocyanate-reactive blend can be calculated by weighting each contribution as such:

P700 contribution – 90% of 2.62 HLB; TEOA contribution - 10% of 20 HLB

Therefore: [(90*2.62)+(10*20)]/100 = Average HLB = 4.4 HLB → Lipid soluble

Note: All other isocyanate-reactive blends studied using PEG-400 and TRI-625 and glycerol have HLB of 20 accounting for the fully hydrophilic portions in their composition