

# Powder Liquid Dispersions of Plasticizers to Increase Throughput and Meet Sustainability Goals for Tire Tread Formulations

Dejan Andjelkovic\*, Bradley Pentzien, Stephen O'Rourke

Industrial Solutions  
The Hallstar Company  
5851 West 73<sup>rd</sup> Street  
Bedford Park, IL 60638

Presented at the Fall 192<sup>nd</sup> Technical Meeting of Rubber Division, ACS  
Cleveland, OH  
October 10-12, 2017

ISSN: 1547-1977

## ABSTRACT

Sustainability metrics continue to evolve as businesses strive for reductions in carbon footprint. The addition of liquids to rubber compounds leads to handling, incorporation and dispersion issues resulting in increased energy consumption. Despite these problems, many compounders incorporate various liquid additives, ranging from low viscosity oils to viscous, tacky polymers. In large volume applications like tires, the installation of storage tanks and metering pumps can solve the handling problems but at significant cost. Given the need for improved consistency, more rapid incorporation, and overall decreased energy consumption, we argue that the use of a powder liquid dispersions (PLD) provides significant value.

In a PLD, the liquid is absorbed onto a suitable powder (or carrier) to form a product with the appearance of a powder, but which contains a high proportion of liquid. During mixing, the shear force will break down the structure of the carrier so that the liquid is gradually released into the mix, resulting in rapid dispersion.

We will use tire tread formulations to confirm that physical data are not affected by a shift from liquid plasticizers to powder liquid dispersions. Additionally, mixing time, torque, and energy consumption will be addressed to emphasize the efficiency and sustainability gains realized from incorporation of PLDs.

## INTRODUCTION

The tire tread compounding process typically starts by breaking down polymers (elastomers) in an internal mixer, sometimes with the aid of peptizer additives. The outcome of this initial stage is the reduction of polymer molecular weight. This step is then followed by the addition of plasticizers, carbon black or silica, and oils. Third step typically involves the addition of the balance of fillers and antioxidant, while the last step concludes with the addition of vulcanization components to complete the compound formulation.

Rubber mixing processes typically occur at high temperatures, up to 180°C. During the past several decades, rubber mixing process for tire treads has shifted away from open mill processing and toward internal mixer compounding. This led to increased automation, efficiency, quality, compound uniformity and cost savings. Compounding processes are purposely designed to yield uniform dispersion of all compounding materials in a tire tread formulation.

Detailed design of mixing cycles and order of addition of raw materials are typically governed by a set of well-known guiding principles:<sup>1</sup>

1. Separate high-tack resins from dry powders
2. Hold the batch drop temperature above the  $T_g$  of the hard resin component
3. Contain liquids to prevent leakage and raw material losses
4. Make use of the shear properties of rubber to accelerate mixing, and
5. Avoid scorch and subsequent formation of cured/crosslinked particles and crumb.

In the last several years, the top three principles had been further addressed by the incorporation of dry powder-liquid dispersions (PLD), such as Suprmix<sup>®</sup>. The cycle time advantages of utilizing powder-liquid dispersions with two roll mill mixing is well known in the rubber mixing industry. Liquids such as plasticizers, process aids, tackifiers, co-agents and other additives are thought to disperse into rubber compounds faster and more efficiently when they are added in a powder form. The effects of utilizing Suprmix<sup>®</sup> forms of liquid plasticizers were compared to the addition of the same active ingredient in a liquid form. Significant improvements were noted in both mix cycle times and energy consumption.

Suprmix<sup>®</sup> dispersions are liquids that are typically dispersed on amorphous silica or calcium silicate powder carriers. The powders are low dust, free flowing mixtures that contain between 50 and 80% active ingredient. Most typically the SUPRMIX<sup>®</sup> dispersions contain 72% liquid. The liquids may be solid at room temperature, but are melted for dispersing on the carrier powder. Some typical active ingredients are ester plasticizers, coumarone-indene resin, epoxy resins, waxes, petrolatum, liquid polymers, anti-oxidants, peptizers, co-agents, process oils, adhesion promoters and more. The Suprmix<sup>®</sup> dispersions are used to improve handling, improve batch-to-batch consistency, reduce employee exposure, limit spill potential, improve batch incorporation, reduce equipment clean out, and reduce packaging and residual chemical disposal. Suprmix<sup>®</sup> dispersions used in low melt pre-weighs further improve handling, efficiency and quality.

In one of our earlier collaborative studies with a major rubber compounder, we showcased comparative data on a proprietary nitrile compound utilizing 30 parts of liquid dioctylphthalate (DOP) versus the same recipe utilizing the Suprmix<sup>®</sup> version of DOP.<sup>2</sup> The compound made with the liquid plasticizer required a cycle time of ten minutes, while the cycle time for the compound utilizing the Suprmix<sup>®</sup> was reduced to 7 minutes (Table 1). Data highlighted an approximate 30% improvement in cycle time by utilizing the Suprmix<sup>®</sup> powder versus the liquid, along with approximately 28% reduction in the maximum energy requirements for the compounding process.

Furthermore, in an actual plant setting the same proprietary compound formulations with liquid and Suprmix<sup>®</sup> DOP plasticizer versions exhibited mix times of 210 and 90 seconds respectively. Due to the significant production volume of this compound, the producer was able to increase its plant output and delay the purchase of new mixing equipment.

## TEST METHODS

The compounds for performance testing were mixed in a BR Banbury internal mixer following standard mixing procedures. Curatives were withheld from the Banbury charge and added on a two-roll, 611 x 1311 laboratory mill during finishing operations. Test specimens for compound performance properties were molded at 180 °C for 10 minutes at 5.75 MPa on the sheet surface. Specimens for original properties, low temperature testing, and air oven aging were die-cut from molded sheets.

<b>Mooney Viscometer</b>	ASTMD1646-94, viscTECH+, large rotor, 1 minute Preheat; 121°C (250°F)
<b>Oscillating Disc Rheometer</b>	ASTM D2084-93, RheoTECH Rheometer, round die, 3°; 170°C (338°F) Arc, 30 sec preheat. MH at central point of torque rise, rate – one lb., 2.5 cm / 5 min
<b>Original Properties</b> Tensile, Elongation, Modulus	ASTM D412-92, Method A, Die C, Crosshead speed 51.0 cm/min
Hardness	ASTM D2240-91, 1s reading
Specific Gravity	ASTM D792-91
Brittle Point	ASTM D1053
<b>Air Oven Aging</b>	ASTM D573-81
<b>Fluid Extractions</b>	ASTM D471-06

## RESULTS

Four test formulations were prepared in an intermeshing internal mixer and each formulation was mixed in triplicates. Formula #1, which contained the liquid dioctyl terephthalate (DOTP) plasticizer, was compared to an identical formula #2, which contained the Suprmix<sup>®</sup> version of the same ester plasticizer (Table 2). Note that 41.6 grams of Suprmix<sup>®</sup> DOTP in formula #2 equals the sum of separately added silica (11.6 grams) and liquid DOTP (30 grams) components in formula #1. Both formulations were based on proprietary customer formulations, so Table 2 only lists basic components rather than specific raw materials used. The rotor speed of the mixer remained constant throughout the compounding of all 6 batches; 3 batches of formula #1 and 3 batches of formula #2. Mixing of each batch was stopped once the target temperature of a compound was achieved. Mix cycle times were recorded, while the motor load data were collected once per second throughout the mix cycle.

Summary of the comparative mix times and energy requirements for NBR-DOTP compounds is shown in Table 3. Comparisons between formula #1 and formula #2 indicate an average mix cycle time reduction of 3.9% and power reduction of 4.2% when Suprmix<sup>®</sup> version of the plasticizer is employed.

Formulas #3 and #4 were also mixed in triplicates and compared. The formula compositions are shown in Table 4. Mix parameters were held constant and the mix concluded at a set target temperature. Cycle time and power data are shown in Table 5. Results of this test study demonstrate that there was 27% improvement in mix cycle time and 16.2 % reduction in energy consumption.

Both examples align well with our earlier time and energy output data<sup>2</sup> to further support claims of advantages of using PLDs versus liquid plasticizers. The ability to customize the size of pre-weight packages further simplifies the utility and handling of PLDs in rubber compounds. Some of the many advantages of using PLDs include:

- a) Elimination of the handling problems associated with high viscosity liquids and semi-solids by converting them to a powder form
- b) Elimination of the need for heated inventory storage of high viscosity liquids or non-pouring liquids
- c) Reduction in batch preparation time
- d) Reduction in equipment clean-up time
- e) Improvement in batch incorporation time and raw material dispersion
- f) Reduction in the amount of costly materials wasted when viscous liquids and semi-solids cling to the walls and bottoms of drum packages
- g) Improvement in package disposability by using fiber drums or paper bags as standard packages

These benefits lead to increase in productivity and profitability for rubber compounders. The amount of active material loaded onto a dry powder carrier can vary. Suprmix<sup>®</sup> PLDs typically contain 72% active materials, but custom-sized loading levels are also available. Standard Suprmix<sup>®</sup> PLD's used for tire formulations incorporate 27% non-reinforcing silica as their carrier. This incremental addition of silica has minimal effect on physical properties of the cured rubber.

To demonstrate that these differences are small, we conducted a side-by-side evaluation of tire compound formulations prepared using liquid StarTread<sup>®</sup> plasticizers listed in Table 6 and their PLD analogues. Table 7, on the other hand, lists components used in selected tire tread formula. Formulations are kept constant and the only variable was liquid StarTread<sup>®</sup> plasticizer versus its 72% active PLD analogue. We also want to point out that the total weight of the liquid compound formulations was 237.4 g while that of the PLD analogues was 243.72g. The difference in weight is due to the excess of non-reinforcing silica carried over in the PLDs, while the amount of liquid StarTread<sup>®</sup> plasticizer in each formulation was kept the same at 16.25 grams (i.e.  $22.57\text{g of PLD} \times 0.72 = 16.25\text{g of liquid plasticizer}$ ). Furthermore, the 6.32 grams of excess of non-reinforced silica (i.e.  $22.57\text{g of PDL} \times 0.28 = 6.32\text{g}$ ) in PLD compound formulations accounts for 2.6% of the weight of the total PLD formulation. Considering the total weight % of the fillers in the liquid plasticizer formula (39.09%), the excess of non-reinforced silica from the Suprmix<sup>®</sup> in the PLD formulations raises the level of filler by only 1.58 weight % to a total of 40.67 weight %.

All compounded formulations were molded and tested side-by-side. Table 8 lists comparative Mooney and ODR viscosity data, original and aged physical properties, and fluid resistance data. Results for each pair of liquid StarTread<sup>®</sup> and PLD formulations exhibit small performance differences which indicate that end-users could easily replace liquid additives in their tire formulation with their PLD analogues without a fear of drastic performance changes.

It is evident that PLD versions of liquid rubber additives show significant improvement in mix cycle times and in total power consumption. In addition to positive impacts on the cycle time and energy consumption, the use of PLDs also has significant positive impact on the environment. For instance, the U.S. Department of Energy estimates that coal power plants generate approximately 2.1 lbs. of carbon dioxide (CO<sub>2</sub>) per kilowatt hour (kWh) of electricity produced. Estimating a reduction of 2.15 kWh per batch based on the mix data presented above, a rubber mixing facility that produces 40,000 batches per year would save 86,000 kWh's. This would further translate to a reduction of approximately 180,600 lbs of carbon dioxide.

In March of 2007 the European Council approved proposals that include the reduction of greenhouse gas emissions by 20% by 2020 and reduction of carbon emissions from primary sources by 50% by 2050 versus 1990 levels. The Obama administration had proposed the reduction of emissions levels by 14% by 2020 and by 83% by 2050.<sup>3</sup> Regardless of the recent decision by the Trump administration to cease all implementation of the Paris Accord and the nationally determined contributions to the Paris Accord and the Green Climate Fund,<sup>4</sup> major US cities, states, companies and other organizations continue to stay committed to the Paris Climate Agreement goals.<sup>5,6</sup> Organizations that reduce their carbon footprint will have a competitive advantage in the future. Incorporating liquids by utilizing PLDs, such as Suprmix<sup>®</sup> powders, is a simple way to reduce energy costs, improve mix cycle times and reduce an organizations carbon footprint.

## ACKNOWLEDGEMENTS

Hallstar Industrial Solution team would like to express our appreciation to Gates Corporation team in Galesburg, IL and Hexpol Compounding team in Burton, Ohio, for collaboration, guidance and support on this project.

## REFERENCES

1. F. J. Kovac and M. B. Rodgers, “Tire Engineering” in Science and Technology of Rubber, J. E. Mark, B. Erman and F. R. Eirich, Ed. San Diego: Academic Press, 1994, Ch. 14, pp. 713-714.
2. “Improved Processing and Batch Time Reduction Through Powder Liquid Dispersions, Stephen. O’Rourke, Hallstar Innovations Corporation; [https://www.hallstar.com/webfoo/wp-content/uploads/Improved\\_Processing\\_with\\_Powder\\_Dispersions1.pdf](https://www.hallstar.com/webfoo/wp-content/uploads/Improved_Processing_with_Powder_Dispersions1.pdf)
3. “Not all Senators warming to Obama cap and trade emissions proposal”, Walter Alarkon, TheHill.com
4. Statement by President Trump on the Paris Climate Accord – White House Briefings - <https://www.whitehouse.gov/the-press-office/2017/06/01/statement-president-trump-paris-climate-accord>
5. Cities, States and Companies Vow to Stick to the Paris Climate Agreement - <http://foreignpolicy.com/2017/06/02/cities-states-and-companies-vow-to-stick-to-the-paris-climate-agreement/>
6. Al Gore, “An Inconvenient Sequel – Truth to Power”, published by Rodale, New York, 2017

Rheomix 600 Parameters (77 rpm, 93°C)	DOP	Suprmix® DOP
Plasticizer level (phr)	30	30
Maximum Torque (m.kg)	2.08	2.40
Compound Temperature (°C)	108	111
Maximum Energy (kJ)	64	46
Dispersion Time (min)	10.0	7.0

Table 1. DOP/Nitrile rubber compounding parameters

DOTP Formulations (parts)	Formula #1 (DOTP)	Formula #2 (Suprmix® DOTP)
NBR	100	100
Carbon Black	75	75
Hard Clay	80	80
Silica	11.6	
DOTP	30.0	
Suprmix® DOTP		41.6
TOTAL	296.6	296.6

Table 2. DOTP Formulation

DOTP FORMULA	Mix Time (s)	kWh
#1 - Liquid	291.3	35.3
#2 - Suprmix <sup>®</sup>	280.0	33.8
Δ	11.3	1.5
Δ%	3.9%	4.2%

Table 3. Mixing time and energy requirements data

DBEEA Formulations (parts)	Formula #3 (DBEEA)	Formula #4 (Suprmix <sup>®</sup> DBEEA)
NBR/PVC (70/30) blend	142.8	142.8
Carbon Black	35.0	35.0
Hard Clay	85.0	85.0
Silica	21.8	
DBEEA	56.0	
Suprmix <sup>®</sup> DBEEA		77.8
TOTAL	340.6	340.6

Table 4. Mixing time and energy requirements data

DBEEA FORMULA	Mix Time (s)	kWh
#3 - Liquid	323.7	17.2
#4 - Suprmix <sup>®</sup>	236.3	14.4
Δ	87.3	2.8
Δ%	27.0%	16.2%

Table 5. Mixing time and energy requirements data

Ester Product	Highlighted performance advantages in tire-tread compounds
StarTread <sup>®</sup> A-140	Good Winter, Excellent Wet, Excellent Roll Resistance
StarTread <sup>®</sup> A-200	Good Winter, Good Wet, Good Roll Resistance
StarTread <sup>®</sup> A-400	Excellent Winter Traction, Poor Wet, Good Roll Resistance
StarTread <sup>®</sup> A-700	Good Winter, Excellent Wet, Good Roll Resistance
StarTread <sup>®</sup> A-900	Poor Winter / Roll, Excellent Wet Resistance

Table 6. Esters for tire tread compound formulations and their performance strengths



	StarTread ® A-200	StarTread ® A-400	StarTread ® A-700	StarTread ® A-900	TDAE oil	PLD of StarTread ® A-200	PLD of StarTread ® A-400	PLD of StarTread ® A-700	PLD of StarTread ® A-900	PLD of TDAE oil
Material	Parts (phr, wt.)					Parts (phr, wt.)				
Duradene 739 S-SBR	75.00									
Diene 645 BR	25.00									
Hi-Sil 190G (silica)	80.00									
X 50-S (reinforcing agent)	12.80									
Norman-346 (TDAE oil)	16.25									
Kadox 920 (zinc oxide)	2.50									
Stearic acid	1.00									
Antiozonant Vulkanox 4020 (6PPD)	2.00									
Nochek 4729 (paraffin wax)	1.50									
StarTread® A-200	16.25	---	---	---	---	22.57	---	---	---	---
StarTread® A-400	---	16.25	---	---	---	---	22.57	---	---	---
StarTread® A-700	---	---	16.25	---	---	---	---	22.57	---	---
StarTread® A-900	---	---	---	16.25	---	---	---	---	22.57	---
TDAE oil	---	---	---	---	16.25	---	---	---	---	22.57
Subtotal:	232.30	232.30	232.30	232.30	232.30	238.62	238.62	238.62	238.62	238.62
Mill Addition										
Sulfur	1.40					1.40				
Vulkacit CZ (sulfenamide)	1.70					1.70				
Akrochem Accelerator DPG (diphenylguanidine)	2.00					2.00				
Total:	237.40	237.40	237.40	237.40	237.40	243.72	243.72	243.72	243.72	243.72

Table 7. StarTread® liquid and PLD tire compound formulations

	1	2	3	4	5	6	7	8	9	10
	StarTread ® A-200	StarTread ® A-400	StarTread ® A-700	StarTread ® A-900	TDAE oil	PLD of StarTread ® A-200	PLD of StarTread ® A-400	PLD of StarTread ® A-700	PLD of StarTread ® A-900	PLD of TDAE oil
<b>Viscosity and Curing Properties</b>										
<b>Mooney Viscosity at 121°C</b>										
Minimum Viscosity	62.6	56.9	49.0	56.3	68.4	53.6	71.1	55.0	69.0	88.8
t5, minutes	28.7	22.7	34.5	26.6	13.2	33.7	11.6	33.7	24.7	15.2
t10, minutes	35.0	29.9	41.1	32.5	16.4	39.3	13.5	40.7	30.0	17.4
t35, minutes	50.8	57.9	56.4	45.0	22.4	53.1	18.2	56.4	42.0	22.4
<b>Oscillating Disc Rheometer at 170°C</b>										
M <sub>L</sub>	14.7	12.0	12.0	11.7	14.4	13.7	16.1	13.6	14.8	19.9
M <sub>H</sub>	73.0	66.3	81.1	84.9	66.1	87.8	67.0	80.8	86.2	68.8
t <sub>0.2</sub> , minutes	1.8	1.6	2.3	2.0	1.5	2.4	1.4	2.3	2.1	1.5
t'c(90), minutes	24.7	27.6	23.0	26.0	19.6	18.9	24.4	22.6	25.2	23.5
1.25 * t'c(90), minutes	30.9	34.6	28.7	32.5	24.5	23.7	30.5	28.2	31.5	29.4
Cure Rate Index	4.4	3.8	4.8	4.2	5.5	6.1	4.4	4.9	4.3	4.6
<b>Original Physical Properties</b>										
Stress @ 100% Elongation, MPa	3.3	3.0	3.3	4.0	3.1	3.5	3.1	3.7	4.4	3.7
Stress @ 100% Elongation, psi	475	430	475	575	450	510	455	540	635	540
Stress @ 200% Elongation, MPa	8.1	6.9	7.2	8.7	7.5	7.1	7.1	7.9	9.3	7.0
Tensile Ultimate, MPa	13.6	13.1	12.9	12.3	13.8	17.3	12.8	12.5	14.1	14.7
Tensile Ultimate, psi	1975	1905	1870	1790	1995	2515	1855	1815	2050	2135
Elongation @ Break, %	290	310	305	265	300	430	320	340	275	420
Hardness Duro A, pts.	68	70	78	77	67	80	71	77	76	74
Specific Gravity	1.203	1.189	1.206	1.220	1.193	1.216	1.198	1.219	1.233	1.206
<b>Aged Vulcanizate Properties</b>										
<b>Air Oven Aging, 168h @ 100°C</b>										
Stress @ 100% Elongation, MPa	6.2	4.7	6.2	5.3	3.1	5.2	3.8	5.1	4.6	3.9
Stress @ 100% Elongation, psi	900	675	900	850	760	970	745	835	955	855
Stress Change, %	89	57	89	48	69	90	64	55	50	58
Tensile Ultimate, MPa	10.1	10.1	11.8	12.7	10.1	12.5	11.3	11.0	13.3	9.7
Tensile Ultimate, psi	1465	1470	1715	1840	1465	1820	1640	1595	1925	1400
Tensile Change, %	-26	-23	-8	3	-27	-28	-12	-12	-6	-34
Elongation @ Break, %	200	260	235	270	210	220	260	240	235	190
Elongation Change, %	-31	-16	-23	2	-30	-49	-19	-29	-15	-55
Hardness Duro A, pts.	76	79	86	85	77	87	81	87	84	83
Hardness Change, pts.	8	9	8	8	10	7	10	10	8	9
Weight Change, %	-2.9	-3.7	-3.7	-2.9	-2.5	-2.9	-3.4	-3.7	-2.8	-2.7
<b>Fluid Resistance</b>										
<b>Distilled Water, 70h @ 100°C</b>										
Stress @ 100% Elongation, MPa	3.8	3.6	5.2	5.3	3.1	5.2	3.8	5.1	4.6	3.9
Stress @ 100% Elongation, psi	555	525	760	775	450	750	555	735	670	570
Stress Change, %	17	22	60	35	0	47	22	36	6	6
Tensile Ultimate, MPa	11.1	12.3	12.7	12.2	12.2	14.9	11.7	11.7	13.1	11.7
Tensile Ultimate, psi	1610	1790	1845	1775	1765	2155	1690	1700	1900	1700
Tensile Change, %	-18	-6	-1	-1	-12	-14	-9	-6	-7	-20
Elongation @ Break, %	325	260	250	210	410	285	275	310	350	360
Elongation Change, %	12	-16	-18	-21	37	-34	-14	-9	27	-14
Hardness Duro A, pts.	77	74	85	85	69	88	78	87	83	78
Hardness Change, pts.	9	4	7	8	2	8	7	10	7	4
Volume Change, %	-0.2	2.3	-0.6	2.5	1.9	0.1	2.5	-0.4	2.1	2.4
Weight Change, %	0.3	2.4	0.0	2.2	2.3	0.8	2.8	0.3	2.0	2.7

Table 8. StarTread® liquid versus PLD tire compound data