

# Ultra High-Performance Elastomers Based on Trans-Bis(Isocyanatomethyl Cyclohexane)

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## ABSTRACT

Polyurethane elastomer systems based on the new aliphatic diisocyanate, trans-bis(isocyanatomethyl cyclohexane) also referred to as trans-1,4-H6XDI (trans-1,4-hydrogenated xylylene diisocyanate) will be introduced. This new aliphatic diisocyanate has a very compact, linear and symmetrical structure which results in ultra high-performance properties. In particular, the resilience and tear strength are superior or comparable to other ultra high-performance elastomers based on para-phenylene diisocyanate (PPDI) and o-tolidine diisocyanate (TODI). Being aliphatic, isocyanate prepolymers based on trans-1,4-H6XDI have superior stability in regards to shelf life, heat history and exposure to humidity. Isocyanate prepolymers may be processed with short chain diols such as 1,4-butanediol or aromatic diamines with a wide range of pot life. Elastomers based on trans-1,4-H6XDI have superior light stability resulting in parts that retain their color over a longer period of time than elastomers based on aromatic diisocyanates. This technical paper will present the physical/mechanical properties, thermal mechanical behavior and abrasion resistance properties. Results will show that elastomers based on trans-1,4-H6XDI offer ultra high-performance properties.

## INTRODUCTION

The two major classes of cast polyurethane elastomers are those based on MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate). These two classes of elastomers give properties which meet or exceed the requirements of a majority of applications. However, there are applications which require extra dynamic performance, abrasion resistance or other properties which cannot be met by MDI and TDI-based elastomers. For these types of applications, ultra high-performance elastomers based on NDI (naphthalene diisocyanate), PPDI (para phenylene diisocyanate) or TODI (o-tolidine diisocyanate) are used.<sup>1-5</sup> These type of elastomers have superior dynamic performance and excellent tear and abrasion resistance.

For applications which require light stability, none of the above diisocyanates will meet that requirement since they are aromatic diisocyanates. Polyurethane elastomers that are made with aromatic diisocyanates will yellow over time when exposed to light. For light stable applications, one needs to use an aliphatic diisocyanate such as H12MDI (dicyclohexylmethane diisocyanate) or IPDI (isophorone diisocyanate). However, elastomers based on H12MDI or IPDI have inferior dynamic performance. So there is a market need for an ultra high-performance diisocyanate which is aliphatic.<sup>6</sup> A new aliphatic diisocyanate has been developed and commercialized by Mitsui Chemical. It is called Fortimo™ 1,4-H6XDI (trans-1,4-hydrogenated xylylene diisocyanate) which will be referred to as trans-1,4-H6XDI. This technical paper will present the physical/mechanical properties, thermal mechanical behavior and abrasion resistance properties of elastomers based on trans-1,4-H6XDI.

## RESULTS AND DISCUSSION

### Ultra High-Performance Diisocyanates

Figure 1 illustrates the current commercially available ultra high-performance diisocyanates: NDI, PPDI and TODI. As one can see from the structures of these diisocyanates, they are all very compact, linear and symmetrical with respect to the isocyanate groups. They are also all aromatic diisocyanates. Recently, Mitsui Chemical has introduced a new aliphatic

diisocyanate called Fortimo™ 1,4-H6XDI which is shown in Figure 2. The structure of trans-1,4-H6XDI is very compact like the other ultra high-performance diisocyanates, but is aliphatic. Since it is enriched in the trans isomer, it has a very linear and symmetrical structure with respect to the isocyanate groups. It is a clear water-white liquid at room temperature with an equivalent weight of 97.2 g/eq. It has a vapor pressure lower than PPDI and TDI, but slightly higher than NDI and IPDI.

Figure 1: Chemical Structures of NDI, PPDI and TODI

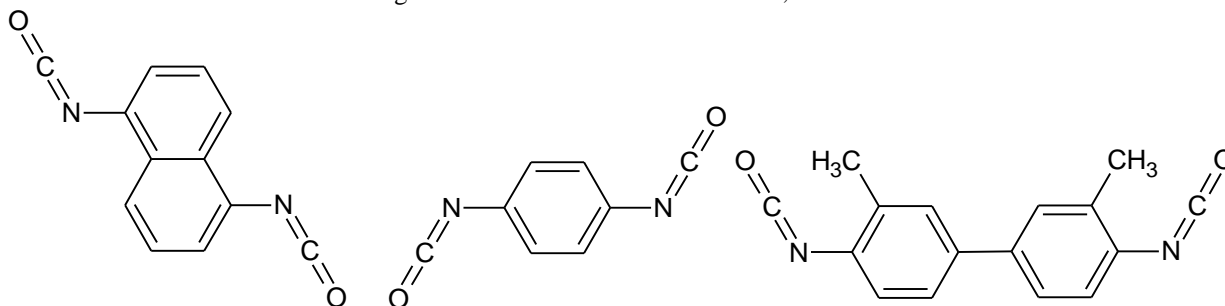
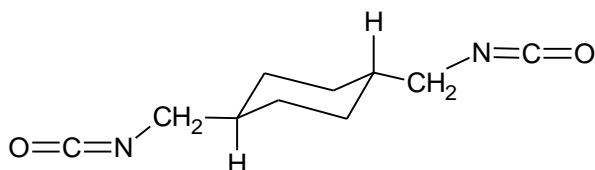


Figure 2: Chemical Structure of trans-1,4-H6XDI



### Prepolymers Based on trans-1,4-H6XDI versus other Ultra High-Performance Diisocyanates

Prepolymers were prepared with trans-1,4-H6XDI using a 2000 MW polycaprolactone (PCL-2000). Table 1 shows a comparison of the trans-1,4-H6XDI prepolymer to ones based on PPDI and TODI. These prepolymers were designed to give a 93 Shore A hardness using 1,4-butanediol as a chain extender.

Table 1: Ultra-High Performance Diisocyanate Prepolymers Based on 2000 MW Polycaprolactone

Diisocyanate	% NCO	Prepolymer Viscosity (cps) @			
		70°C (158°F)	80°C (176°F)	90°C (194°F)	100°C (212°F)
trans-1,4-H6XDI	7.8	830	570	420	350
PPDI	4.1	2300	1600	1150	950
TODI	6.3	2550	1580	1060	750

As one can see from the data above, the trans-1,4-H6XDI prepolymer has a lower viscosity than those based on PPDI and TODI, however, all of these prepolymers are well within the processability limits (2000 cps maximum @ 100°C) of a typical cast elastomer operation. Conventional trans-1,4-H6XDI prepolymers and TODI prepolymers are easier to process than conventional PPDI prepolymers in that PPDI will sublime and coat itself on the interior of the container surfaces above the liquid level. The sublimed PPDI monomer can build up over time making it a challenge to keep equipment from fouling. Trans-1,4-H6XDI prepolymers, having aliphatic isocyanate groups, are much less reactive with moisture in the air, so they have much less of a tendency to skin over than PPDI or TODI based prepolymers. Additionally, trans-1,4-H6XDI prepolymers have a much less of a tendency to form allophanate crosslinks so they have a much longer shelf life at ambient temperature and are much more stable at elevated processing temperatures. Shelf life and stability are of particular importance when using high-value, ultra high-performance prepolymers.

### Prepolymer Processability of trans-1,4-H6XDI Prepolymers versus other Ultra High-Performance Diisocyanates

The above prepolymers were chain extended with 1,4-butanediol to make polyurethane elastomers. Table 2 shows the pot life and demold time using these prepolymers without catalyst. The prepolymers were processed at 180°F (85°C) and the 1,4-butanediol was at room temperature.

Table 2: Uncatalyzed Prepolymer Processing Characteristics using 1,4-Butanediol

Diisocyanate Prepolymer	Pot Life (minutes)	Demold time (minutes)
trans-1,4-H6XDI	20	>240
PPDI	7	60
TODI	15	90

As expected, the prepolymer based on trans-1,4-H6XDI had the longest pot life at 20 minutes, but also had the longest demold time of greater than 240 minutes. This was followed by the TODI prepolymer with a 15 minute pot life and a demold time of 90 minutes and then the PPDI prepolymer with a pot life of 7 minutes and the shortest demold time of 60 minutes. The general trend is the longer the pot life, the longer the demold time.

In typical casting operations, one would catalyze these prepolymers to achieve a shorter demold time. Table 3 shows the effect of catalyst on the pot life and demold time of these prepolymers. Triethylene diamine (TEDA) was used as a catalyst for the PPDI and TODI prepolymers and dibutyltin dilaurate (DBTDL) was used for the trans-1,4-H6XDI prepolymer. A mold temperature of 240°F (116°C) was used for all three systems.

Table 3: Catalyzed Prepolymer Processing Characteristics using 1,4-Butanediol

Diisocyanate Prepolymer	Catalyst Type	Catalyst Amount (ppm)	Pot Life (minutes, seconds)	Demold Time (minutes)
trans-1,4-H6XDI	DBTDL	100	6 to 10	60
		200	3 to 5	40
		300	1.5 to 2.5	20
PPDI	TEDA	200	4 to 6	45
		400	1.5 to 2	30
TODI	TEDA	200	5 to 7	45
		400	2 to 4	30
		800	1.25 to 1.75	15

As shown from the data above, the pot life along with the demold time can be reduced easily by using catalyst. For the aromatic diisocyanate prepolymers (PPDI and TODI), the amine catalyst, triethylene diamine (TEDA) is the preferred catalyst since one can use a relatively sizable amount (200 to 800 ppm). Whereas, if one used a metal catalyst like dibutyltin dilaurate (DBTDL) then one would have to use amounts in the 5 to 20 ppm range which is very difficult to add and control. For the trans-1,4-H6XDI prepolymer one has to use a metal catalyst since amine catalyst are not very effective with aliphatic isocyanates. Using DBTDL catalyst in the range of 100 to 300 ppm gives a very workable range of pot life from 1.5 to 10 minutes. Please note it is generally known that a shorter pot life with these ultra high-performance elastomer systems results in better processability (improved green strength) and a reduced demold time. This will be discussed in more detail in the section regarding the effect of catalyst and mold temperature on the elastomer properties.

#### **Elastomer Physical/Mechanical Properties Based on trans-1,4-H6XDI versus PPDI and TODI**

The physical/mechanical properties of the 93A elastomers based on trans-1,4-H6XDI, PPDI and TODI are shown in Table 4. These elastomers were cast using a prepolymer temperature of 180°F (85°C) using 1,4-butanediol as curative at room temperature. They were catalyzed to a pot life of 2 minutes using DBTDL for the trans-1,4-H6XDI and TEDA for the PPDI and TODI systems. The mold temperature was 240°F (116°C). The elastomers were demolded and then post cured overnight at 212°F (100°C) for about 16 hours. The elastomer plaques were conditioned at 73°F (23°C) and 50% humidity for at least two weeks prior to testing the physical/mechanical properties. The compression sets were determined after at least four weeks conditioning.

Table 4: Physical/Mechanical Properties of Elastomers based on trans-1,4-H6XDI, PPDI and TODI, 2000 MW Polycaprolactone Prepolymers cured with 1,4-Butanediol

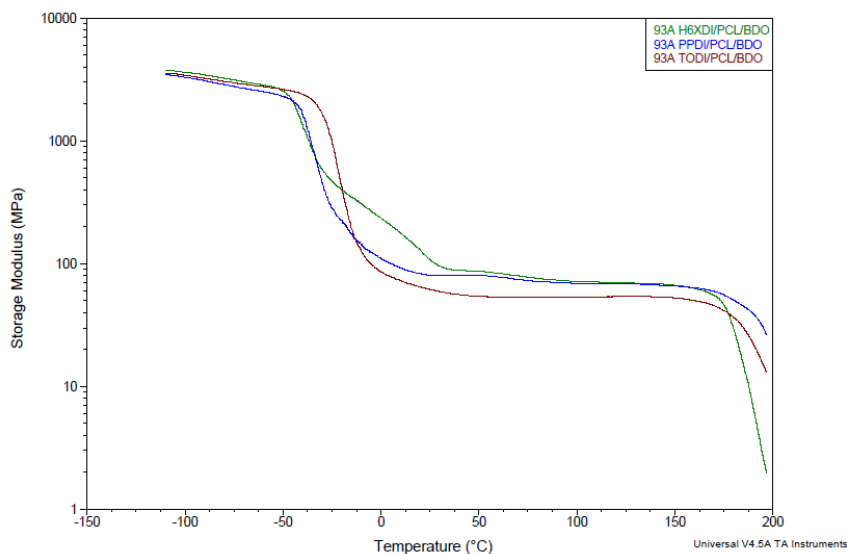
	trans-1,4-H6XDI	PPDI	TODI
Hardness, Shore	93A	93A	93A
Elongation, %	760	580	650
Tensile Strength, psi (MPa)	7400 (51.0)	6100 (42.1)	5000 (34.4)
100% Modulus, psi (MPa)	1370 (9.4)	1300 (9.0)	1200 (8.3)
300% Modulus, psi (MPa)	2000 (13.8)	1800 (12.4)	1600 (11.0)
Die C Tear, pli (kN/m)	650 (114)	590 (104)	570 (100)
Split Tear, pli (kN/m)	490 (86)	400 (70)	440 (77)
Bashore Rebound, %	68	68	57
Compression Set, % (22 hrs @ 70°C)	28	32	28
Abrasion Resistance, (Volume Loss,mm <sup>3</sup> ) ASTM D5963	43	32	88

As one can see from the data above, the trans-1,4-H6XDI elastomer had the highest elongation and also the highest tensile strength. So the area under the stress/strain curve is significantly higher for the trans-1,4-H6XDI elastomer indicating the highest overall toughness. As expected, the 100% modulus for all three elastomers is similar since they are all 93 Shore A hardness. The Die C tear strength is slightly higher for the trans-1,4-H6XDI elastomer, whereas, the PPDI and TODI are comparable. The split tear strength was highest for the trans-1,4-H6XDI followed by the TODI then the PPDI elastomer. The trans-1,4-H6XDI and PPDI had equivalent Bashore rebound at 68% and the TODI based elastomer was significantly lower at 57%. The compression sets of all three elastomers were comparable after 22 hours at 70°C. The abrasion resistance was measured using a rotary drum abrader via ASTM D5963. These results showed that the trans-1,4-H6XDI elastomer has twice the abrasion resistance of the TODI elastomer. This will be compared to the PPDI elastomer in the near future.

### Thermal Mechanical Properties of trans-1,4-H6XDI, PPDI and TODI Based Elastomers

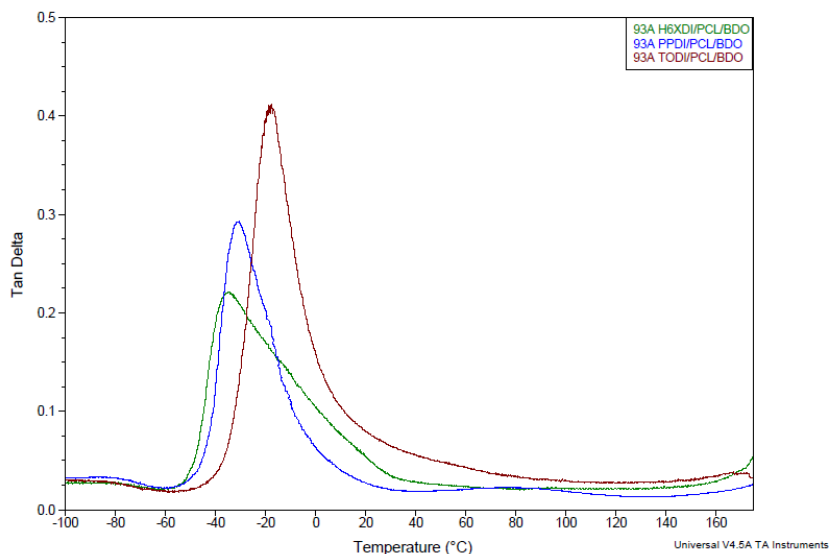
The thermal mechanical properties of the trans-1,4-H6XDI, PPDI and TODI based elastomers were determined using dynamic mechanical thermal analysis (DMTA). An overlay of the storage modulus curves is shown in Figure 3. This figure shows that all three elastomers have a very flat rubbery plateau region. The beginning of the melting transition is comparable for all three elastomers, however, the trans-1,4-H6XDI elastomer drops off more sharply. In the soft segment glass transition area, the trans-1,4-H6XDI elastomer has a significant shoulder which is likely melting of crystallized PCL soft segment.

Figure 3: Storage Modulus Curves for the trans-1,4-H6XDI, PPDI and TODI Elastomers



An overlay of the tan delta curves is shown in Figure 4. The beginning of the tan delta peak is an indication of the brittle point temperature of an elastomer. One can see that the trans-1,4-H6XDI elastomer has the lowest brittle point, closely followed by the PPDI elastomer and then the TODI elastomer. The tan delta peaks show this same trend. The tan delta peak reaches the rubbery plateau at a lower temperature for the PPDI than the trans-1,4-H6XDI. This may be due to some crystallization in the soft segment in the trans-1,4-H6XDI elastomer as suggested previously. The tan delta in the rubbery plateau region is an indication of the heat buildup tendency of the elastomer in a dynamic application. The lower the tan delta, the lower the heat buildup. One can see from the curves that the trans-1,4-H6XDI and PPDI have comparably low tan delta's in the typical temperature use range of polyurethane elastomers, whereas, the TODI elastomer has a significantly higher tan delta. This observation agrees with the lower Bashore rebound or resilience of the TODI elastomer versus the trans-1,4-H6XDI and PPDI elastomers.

Figure 4: Tan Delta Curves for the trans-1,4-H6XDI, PPDI and TODI Elastomers



### Effect of Stoichiometry on the Physical/Mechanical Properties of Elastomers Based on trans-1,4-H6XDI

In this section, the trans-1,4-H6XDI elastomer was cast at three different stoichiometries: 0.91, 0.95 and 0.98. The same processing and curing conditions were used here as the section above. The physical/mechanical properties are shown in Table 5.

Table 5: Effect of Stoichiometry on the Physical/Mechanical Properties of the trans-1,4-H6XDI Elastomer

Stoichiometry	0.91	0.95	0.98
Hardness, Shore	93A	93A	93A
Elongation, %	770	760	750
Tensile Strength, psi (MPa)	7600 (52.4)	7400 (51.0)	6500 (44.8)
100% Modulus, psi (MPa)	1360 (9.4)	1370 (9.4)	1390 (9.6)
300% Modulus, psi (MPa)	1980 (13.7)	2000 (13.8)	1990 (13.7)
Die C Tear, pli (kN/m)	640 (112)	650 (114)	650 (114)
Split Tear, pli (kN/m)	460 (80.7)	490 (86)	520 (91.2)
Bashore Rebound, %	66	68	68
Compression Set, % (22 hrs @ 70°C)	27	28	38

Going from 0.91 to 0.98 stoichiometry did not have much of an effect on the elongation, tensile strength, 100% and 300% modulus, Die C tear strength or Bashore rebound. As expected, it did have a major effect on the split tear strength and compression set. The split tear strength increased by about 15 percent going from 0.91 to 0.98 stoichiometry. The compression set increased slightly going from 0.91 to 0.95 stoichiometry and then increased significantly from 0.95 to 0.98 going from 28% to 38%. The above results indicate that a stoichiometry of 0.95 gives the best overall properties.

## Physical/Mechanical Properties of Lower Hardness trans-1,4-H6XDI/PCL 2000/BDO Elastomers

In this section, the trans-1,4-H6XDI/PCL-2000 prepolymer that was used for the 93A elastomer was cured with blends of PCL-2000 and 1,4-butanediol to achieve a hardness of 86A, 77A and 60A. The same processing and curing conditions were used at a stoichiometry of 0.95. The physical/mechanical properties of these elastomers are shown in Table 6.

Table 6: Physical/Mechanical Properties of trans-1,4-H6XDI/PCL-2000/1,4-BDO Elastomers of Various Hardness

Hardness, Shore	93A	86A	77A	60A
Elongation, %	760	720	750	630
Tensile Strength, psi (MPa)	7400 (51.0)	5400 (37.2)	4900 (33.7)	3200 (22.0)
100% Modulus, psi (MPa)	1370 (9.4)	870 (6.0)	500 (3.4)	290 (2.0)
300% Modulus, psi (MPa)	2000 (13.8)	1470 (10.1)	960 (6.6)	480 (3.3)
Die C Tear, pli (kN/m)	650 (114)	540 (95)	450 (79)	240 (42)
Split Tear, pli (kN/m)	490 (86)	400 (70)	270 (47)	110 (19)
Bashore Rebound, %	68	69	71	80

As expected, the tensile strength decreased with lower hardness, but retained a tensile strength of 3200 psi (22.0 MPa) at a 60 Shore A. Although the Die C and split tear strength decreased with lower hardness, the results of 240 pli (42 kN/m) for Die C and 110 pli (19 kN/m) for split tear on a 60A elastomer is quite exceptional. The Bashore rebound increased with decreasing elastomer hardness going from 68% at 93A to 80% at 60A.

## Physical/Mechanical Properties of Various Hardness trans-1,4-H6XDI/PTMEG-2000/BDO Elastomers

This section highlights the physical/mechanical properties of trans-1,4-H6XDI using 2000 MW polytetramethylene glycol (PTMEG-2000) as a soft segment polyol and 1,4-butanediol as a curative. These elastomer systems used the same processing and curing conditions as those based on 2000 MW polycaprolactone (PCL-2000). Elastomers with hardness of 95A, 85A, 80A and 72A were prepared. The physical/mechanical properties of these elastomers are summarized in Table 7.

Table 7: Physical/Mechanical Properties of trans-1,4-H6XDI/PTMEG/1,4-BDO Elastomers of Various Hardness

Hardness, Shore	95A	85A	80A	72A
Elongation, %	650	760	650	650
Tensile Strength, psi (MPa)	5900 (40.7)	4800 (33.1)	3900 (26.9)	3800 (26.2)
100% Modulus, psi (MPa)	1910 (13.2)	720 (5.0)	560 (3.9)	390 (2.7)
300% Modulus, psi (MPa)	2290 (15.8)	1120 (7.7)	910 (6.3)	630 (4.3)
Die C Tear, pli (kN/m)	620 (109)	420 (74)	360 (63)	240 (42)
Split Tear, pli (kN/m)	360 (63)	90 (16)	75 (13)	45 (8)
Bashore Rebound, %	55	72	74	77

The trans-1,4-H6XDI elastomers based on a PTMEG backbone have excellent overall physical/mechanical properties even at a lower hardness of 80A or less. The tensile strength ranges from 5900 psi (40.7 MPa) to 3800 psi (26.2 MPa), from a 95A down to a 72A hardness. The Die C and split tear was excellent for a polyether based elastomer with values significantly higher than MDI/PTMEG/1,4-BDO elastomers. As expected, the Bashore rebound of these elastomers is very high, indicating that they would be a great candidate for a dynamic application like in-line skate wheels or high-load wheels. As an aside, however, when one compares these Bashore rebound values with those based on the 2000 MW PCL, one can see that the PCL based elastomers are only about two units lower than those based on PTMEG. So trans-1,4-H6XDI elastomers based on PCL essentially have the dynamic properties of a PTMEG-based elastomer, but with the tensile and tear strength, and abrasion resistance of an ester-based elastomer.

## CONCLUSIONS

Elastomer systems based on Mitsui's new aliphatic diisocyanate, Fortimo™ 1,4-H6XDI, exhibit ultra high-performance properties. This new aliphatic diisocyanate has a very compact, linear and symmetrical structure resulting in a superior hard segment with 1,4-butanediol that gives a high melting/softening temperature and great phase separation between the

hard and soft segments. The physical/mechanical properties are superior or comparable to those based on other ultra high-performance diisocyanates like PPDI and TODI, in particular, the resilience (Bashore rebound), tear strength and abrasion resistance. Prepolymers based on trans-1,4-H6XDI have superior stability in regards to shelf life, heat resistance and exposure to humidity. Elastomers based on the aliphatic trans-1,4-H6XDI have excellent light stability resulting in parts that retain their color over a longer period of time than elastomers based on aromatic diisocyanates such as PPDI, TODI or MDI. Trans-1,4-H6XDI elastomers using a 2000 MW polycaprolactone backbone were particularly impressive with the resilience of a PTMEG backbone but the toughness and abrasion resistance of an ester backbone. These results support that elastomer systems based on trans-1,4-H6XDI have the physical/mechanical toughness, thermal/mechanical profile, dynamic performance and abrasion resistance of ultra high-performance elastomers.

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## BIOGRAPHIES

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### Jordan Duckett

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