

# **“Dry Latex.” A New Method for the Preparation of Rubber-Filler Powders**

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## **Synopsis**

A new method of preparing rubber powders, especially masterbatch powders, is described. It consists of the dispersion of polymer latices in highly hydrophobic fine particle-size powders such as special silicas and carbon black, followed by drying. During the whole procedure the powders never lose their pourable state. Several powder properties, e.g., particle size distribution, pourability, bulk density, and angle of repose, are dealt with for NR and SBR powders. These powders require a high shear processing stage to disperse the black and rubber chemicals into the rubber matrix. For direct extruder feeding, a highly efficient extruder mixing screw is necessary. It is shown that the powders can be sufficiently protected against aging by use of special antioxidants. The procedure is characterized by an outstanding simplicity in respect to engineering and equipment. The future outcome of the method will depend on the balance between that simplicity and the energy demand which can be tolerated.

## **INTRODUCTION**

Rubber powders have been paid increased attention during the last ten years in respect to further rationalization of rubber processing. In contrast to liquid rubbers, it is expected that reduced labor and power consumption could be reached during maintenance of most of the existing rubber processing machinery.

A number of methods for the preparation of rubber powders<sup>1</sup> have been developed which are considerably different in respect to practicability, economy, and product quality. Since many negative aspects among those properties are related to the production process itself, a new, simpler process for the preparation of rubber powders was investigated, which is described in this paper.

## **PRINCIPLE OF THE “DRY LATEX METHOD”**

The development of the “dry latex method” arose from observations dealt with by Degussa,<sup>2</sup> namely, that highly hydrophobic silicas are able to incorporate up to 90 wt. % dispersed water without changing the physical state of a free-flowing powder (“dry water”). Microscopic examination of such a dispersion reveals that the small water drops are distributed in a continuous silica matrix. Each water droplet is surrounded by several thousands of silica particles which themselves consist of an aggregation of much smaller primary particles.

Though the stickiness of high-polymer latex was considered to be adverse in a similar application, preliminary experiments exhibited a surprisingly simple and versatile process for the preparation of rubber powders.

Without regard to specific details of the process depending on the fine-particle filler type, latex type, latex solids content, etc., the following stages of the procedure<sup>3</sup> are characteristic in general:

1. Breakup of the hydrophobic fine-particle-size material by a short high-speed stirring operation.

2. Dispersion of the latex into the mechanically agitated hydrophobic powder, preferably by spraying. The dispersing has to be terminated when the latex content has reached a certain level, otherwise the free-flowing powder property is lost and a paste is formed.

3. The resulting still free-flowing powder is dried by conventional methods, preferably by application of both heat and vacuum. Continuous stirring during the drying stage favors the formation of fine-particle-size powders.

Obviously, the hydrophobic nature of the fine particle-size material disperses the latex so that paste formation is delayed until the above-mentioned high concentrations are reached. Nevertheless, to confirm the hypothesis, a series of experiments with hydrophilic fine-particle-size materials, especially silicas, were carried out and always resulted in early formation of pastes.

The first trials following the dry latex concept were directed toward the preparation of powders using highly hydrophobic silicas, where all tested high-polymer latices resulted in a free-flowing powder. The necessary amount of silica depended on the type and concentration of the latex. Thus, for example, 10 wt. % has to be applied with an SBR latex for 60 wt. % solids content (s.c.).<sup>4</sup>

It was a reasonable assumption that not only hydrophobic silicas but also other hydrophobic powders could be applied in the dry latex method. Among several alternatives carbon black was considered the most attractive one for a number of features: (1) small particle size, (2) available in numerous grades, and (3) reinforcing properties for rubber.

Little information was available in the literature on carbon black concerning the essential feature of hydrophobicity.<sup>5</sup> However, trials<sup>6</sup> showed it to be suitable for the dry latex process but less effective than the best hydrophobic silicas.

A powder mixture mainly of carbon black with a small part of hydrophobic silica proved most effective for the preparation of rubber powder masterbatches. In such a case the carbon black and the silica both act as hydrophobic continuous phase with the filler/latex dispersion. After powder processing the carbon black develops its second function, namely, reinforcement.

For further processing these rubber/carbon black masterbatch powders have to be provided with plasticizers and rubber chemicals. These ingredients can already be added to the "wet" powder during the preparation or in the dry state by conventional powder mixing techniques. The latter are preferred since the additives are usually added just before processing to a masterbatch powder that has been previously stored.

In the following, the preparation and properties of some rubber powders, especially of SBR- and NR-based ones, are described. Besides the properties of the powders themselves, their processing behavior and finally the mechanical properties of vulcanizates made from them are also dealt with.

## EXPERIMENTAL RESULTS

The quality of a rubber/filler masterbatch prepared by application of the dry latex method depends on a number of parameters: composition of the starting powder, especially the carbon black/silica ratio; quality of the applied latex, especially its solids content and tackifier content; efficiency of the mixing

equipment used for latex dispersion into the starting powder; and effectiveness of the drying stage. In this connection the term "quality" of the powder implies particle size distribution, composition dependent on particle size, pourability, bulk density, packed bulk density, angle of repose, processing behavior, mechanical properties of vulcanizates, and aging during storage.

A large number of experiments to elucidate the correlation between the above quantities were carried out with available polymer latices such as those from SBR, NR, NBR, and CR. The following examples with SBR and NR restricted to a specific optimal carbon black/silica powder are typical.

### SBR Powders

#### *Preparation*

Hydrophobic silica Aerosil R 972 (Degussa), 7 g, was placed into a high-speed mixer and stirred briefly. Carbon black "Corax 3" (Degussa), 43 g, was then mixed with the silica. The ensuing dispersing stage is the critical phase of the process. A special nozzle was constructed to provide a wide latex spray stream, the speed of which was adjusted in such a way as to prevent overloading by latex in the upper layers of the agitated powder. The tendency to form bigger particles in dead zones of the mixer was largely overcome by a movable frame enabling rotation of the whole mixer. By this means 189 g SBR latex 2116 (from Buna Hüls, originally 24% s.c., concentrated up to 53% s.c.) was added to the mixer and dispersed in the powder for about 2 min. The wet but free-flowing powder was then dried at elevated temperatures in normal laboratory vacuum (in general, 40°C/48 hr) while stirring continuously and slowly.

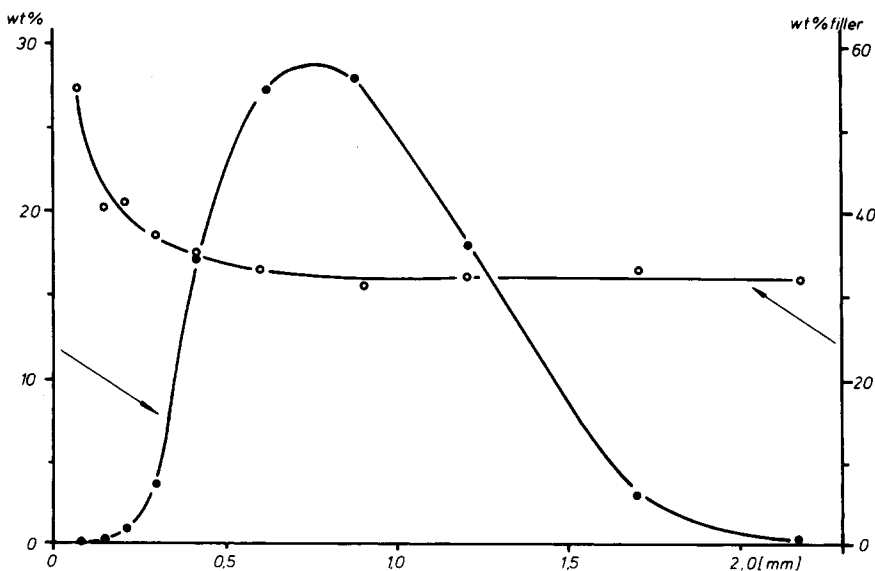


Fig. 1. Distribution of particle size and filler content with SBR masterbatch powders.

TABLE I  
Properties of SBR Powder Masterbatches

	Pourability, sec <sup>a</sup>	Bulk density, g/cm <sup>3</sup> <sup>b</sup>	Packed bulk density, g/cm <sup>3</sup> <sup>c</sup>	Angle of repose, degrees <sup>d</sup>
Total Powder	18.6	0.464	0.50	33
Fractions				
1.0-1.4 mm	23.9	0.424		
0.75-1.0 mm	21.6	0.445		
0.5-0.75 mm	18.6	0.455		
0.35-0.5 mm	16.7	0.474		

<sup>a</sup> Determined by ASTM D1895-69, die 9.5 mm.

<sup>b</sup> Determined by DIN 53468.

<sup>c</sup> Determined by DIN 53194.

<sup>d</sup> See R. L. Carr, *Chem. Eng.*, 163 (Jan. 1965).

### *Powder Properties*

The powders obtained according to this procedure exhibited excellent free-flow properties, even after a storage time of three months.

The particle size distribution, obtained by a conventional sieving technique, is given in Figure 1. It can be seen that the maximum of the distribution function is at about 0.75 mm. Particle sizes > 1.7 mm and < 0.25 mm are below 3 wt. %. The filler content of the respective fractions was determined by pyrolysis gas chromatography and resulted in the second curve in Figure 1. It can be seen that it is nearly independent of the particle size down to 0.5 mm. Only in the very small fractions below 0.2 mm an increased content is found, especially with the smallest particle size. It is thought that this fraction mainly contains filler not used for covering rubber particles.

In Table I some properties important for storage and handling of powders are given. It can be seen that there is a tendency toward improvement of pourability and increase in bulk density with decreasing particle size.

### *Processing Properties*

As a measure of the processing behavior the Mooney viscosity number ML 1 + 4 at 100°C was measured. For the test the powders had first to be compressed by a single mill pass. Thereafter, it measured ML 1 + 4 = 94. It is obvious that this high figure is the result of the incomplete mixing state. To elucidate this in some more detail the powders were passed through a Goettfert table extruder at 120°C. After a single pass, a Mooney viscosity of ML 1 + 4 = 66 was determined. This value decreased to ML 1 + 4 = 58 after four extruder passes.

The extrudability of the powders was tested by passing them through the Goettfert table extruder several times. The conditions of the test were: 100°C, 40 rpm, die 2 mm. The powders were fed directly into the extruder and were accepted without difficulties. The resulting extrudate had a normal cohesion but a poor surface. After a second pass the surface quality was improved to "medium quality," whereas a third and fourth pass resulted in "good surface quality."

This result reflects again the insufficient mixing of the compound during a

single extruder pass and indicates the need for using an effective mixing screw to secure the full advantages of the rubber powder technology.

*Vulcanizate Properties*

To study vulcanizate properties the powders were compounded in a mixing device under addition of plasticizer and rubber chemicals. The composition and cure conditions of the compound are given in Table II. The fully compounded powders were processed on the mill at 70°C for varying lengths of time. After cure most of the important mechanical properties were measured. The results are given in Table III. It can be seen that most mechanical properties approach an optimum after 5 min of milling time, whereas tear strength and resilience are high from the beginning.

**NR Powders**

*Preparation*

The same starting powder as described for SBR was prepared. Then, 125 g NR latex with a solids content of 40% was added by spraying onto the agitated powder surface. After intensive mixing and mixer turnings, again 125 g latex was added. The somewhat spongy agglomerates were treated with 1 wt. % carbon black or hydrophobic silica. Further mixing, again accompanied by steady turning of the whole mixer, resulted in a free-flowing wet powder.

TABLE II  
Formulations of SBR and NR Compounds

		Composition, phr
SBR Compounds		
SBR		100
Corax 3		43
Aerosil R 972		7
Zinc oxide		4
Stearic acid		2
Naftolen ZD		8
Sulfur		1.75
Vulkacit CZ		1.25
PBN		1
4010 NA		1.5
Antilux		0.5
Cure: 160°C/12 min		
NR Compounds		
NR		100
Corax 3		43
Aerosil R 972		7
Naftolen ZD		3
Zinc oxide		5
Stearic acid		3
Sulfur		2.5
Vulkacit CZ		0.5
PBN		1
4010 NA		2
Antilux		0.5
Cure: 143°C/30 min		

TABLE III  
Mechanical Properties of SBR Compounds

	1 min <sup>a</sup>	2 min	5 min	8 min	12 min	16 min
Hardness, Shore A	60	61	60	61	61	59
Tensile strength, NM/m <sup>2</sup>	13.4	20.1	22.9	24.0	25.6	23.9
Elongation at break, %	510	640	600	640	670	650
Modulus, MN/m <sup>2</sup>						
50%	0.8	0.8	0.7	0.7	0.9	0.8
100%	1.6	1.8	1.7	1.7	1.7	1.4
200%	3.3	4.1	3.6	3.8	3.7	3.1
300%	5.6	6.8	6.7	7.2	7.3	6.1
Tear strength, kN/m	26.4	27.6	25.6	24.2	26.4	25.0
Elongation set, %						
15 min	14	16	11	11	12	13
1 hr	6	6	4	6	4	5
Resilience, %	37	32	35	33	30	33

<sup>a</sup> Milling time.

Under steady stirring the powder was dried at 40°C under oil pump vacuum. A period of 6 hr should not be exceeded since after this time a tendency to sticking was observed. A final drying was carried out under vacuum at 40°C for 48 hr without stirring.

#### Powder Properties

The particle size distribution is given in Figure 2. It is seen that the average particle size is 1.1 mm. Particles below 0.2 mm and above 2.5 mm range under 2 wt. %. The filler distribution over the fractions was about 30 wt. %, nearly independent of particle size. There was only again a slight tendency for the filler content to increase toward smaller particle sizes. Other powder properties are given in Table IV.

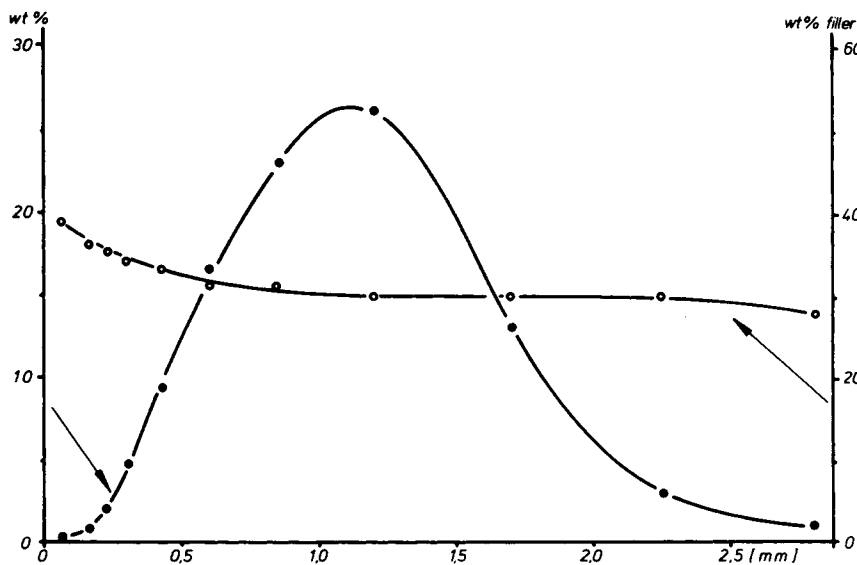


Fig. 2. Distribution of particle size and filler with NR masterbatch powders.

TABLE IV  
Properties of NR Powder Masterbatches

	Pourability, sec <sup>b</sup>	Bulk density, g/cm <sup>3</sup> <sup>c</sup>	Packed bulk density, g/cm <sup>3</sup> <sup>d</sup>	Angle of repose, degrees <sup>e</sup>
Total powder	39.0 <sup>a</sup>	0.347	0.45	41
Fractions				
1.4–2.0 mm	36.0 <sup>a</sup>	0.323	0.41	42
1.0–1.4 mm	36.0 <sup>a</sup>	0.319	0.43	44
0.71–1.0 mm	27.8	0.353	0.45	46
0.5–0.71 mm	24.6	0.361	0.44	43
0.335–0.5 mm	21.4	0.374	0.55	49

<sup>a</sup> The flow of these powders had to be supported by repeated knocking on the funnel.

<sup>b</sup> Determined by ASTM D 1895-69, die 9.5 mm.

<sup>c</sup> Determined by DIN 53468.

<sup>d</sup> Determined by DIN 53194.

<sup>e</sup> See preparation of SBR powders, p. 347.

Again the expected tendency can be seen, namely, that pourability improves and density increases with decreasing particle size.

#### *Processing and Vulcanizate Properties*

Masterbatch powders of the above type and fully compounded ones form a continuously running sheet on the mill after one revolution and can be processed further as usual with the known saving of mixing energy and time.

A direct feeding of the powders to a conventional table extruder at 70°C caused trouble because of the high starting molecular weight of the NR, whereas a temperature of 90°C enabled the preparation of a good extrudate. However, as expected, optimum compound properties were not reached after a single pass since the mixing efficiency of the conventional screw was not sufficient. To demonstrate the possible further improvement of compound properties, the changes brought about by a successively increasing number of passes through the extruder were determined. The results are given in Table V, from which it can be seen that the extrudate reached a good surface quality after the second pass. Die swell and shrinkage approached a maximum after two to three passes and improved then steadily with further processing. Mooney viscosity decreased from the initial figure of 124 down to 72 after the last pass.

Vulcanizate properties, also given in Table V, reveal that the optimum balance of mechanical properties approached a high level after about five passes.

#### **Aging**

Rubber powders have to be transported and stored before finally being used for the production of rubber goods. Especially with NR powders this requirement might imply both a long shipping time and the influence of elevated temperatures. It is obvious that a rubber powder should not alter its essential properties under those circumstances.

On the other hand, it is evident that a fine particle-size powder offers a large surface to oxidative reactions so that reduced aging resistance can be expected

TABLE V  
Properties of Unvulcanized and Vulcanized NR Compounds Extruded at 90°C<sup>a</sup>

	1 <sup>b</sup>	2	3	4	5	6	7	8	
Extrudate surface	accept.	←—————→				good	—————→		
Die swell, %	88	115	107	100	99	91	79	62	
Shrinkage, %	47	54	58	50	50	48	44	38	
ML 1 + 4 100°C	124	98	98	100	88	72	72	72	
Hardness, Shore A	65	69	64	61	60	59	59	59	
Tensile strength, MN/m <sup>2</sup>	17.3	18.2	27.1	31.0	33.3	32.0	30.6	31.5	
Elongation at break, %	280	290	440	480	500	520	520	510	
Modulus, MN/m <sup>2</sup>									
50%	2.4	2.6	1.7	1.7	1.5	1.2	1.2	1.4	
100%	4.8	4.9	3.1	2.9	2.7	2.0	2.1	2.3	
300%	—	—	15.2	15.0	14.4	11.5	12.1	12.8	
Tear strength, kN/m	28.1	35.0	33.5	41.6	47.5	43.0	59.9	49.2	
Impact resilience, %	44	44	45	46	46	45	46	46	

<sup>a</sup> Extruder speed 20 rpm, die 2 mm diameter.

<sup>b</sup> Number of passes.

in comparison with the compact materials, especially with powders based on general-purpose diene rubbers.

It was thought that this contradiction—fine particle-size rubber powder and high aging resistance—has never in the past received adequate consideration, so that the following results of an aging test of the dry latex powders might also be of interest as regards the behavior of other rubber powder types. Though it was borne in mind that the 7 days/70°C aging test is a poor substitution for aging in practice, it was nevertheless applied because of its frequent use in the rubber industry and the availability of data for comparison.

As expected, the rubber powder masterbatches unprotected by antioxidants aged considerably under the conditions of this test (Table VI). In addition, pourability of the powders is worsened by agglomeration caused by stickiness and flow. Also in Table VI the important role of the elevated temperature during

TABLE VI  
Aging of An Unprotected SBR Powder Masterbatch Followed by Reduction of Vulcanizate Properties

	Unaged	23°C/28 days	70°C/7 days
Hardness, Shore A	65	63	71
Tensile strength, MN/m <sup>2</sup>	26.2	22.5	8.2
Elongation at break, %	550	500	310
Modulus, MN/m <sup>2</sup>			
50%	1.8	1.5	2.1
100%	3.2	2.7	3.2
200%	7.2	6.4	5.9
300%	12.5	11.3	7.9
Tear strength, kN/m	24.1	24.8	25.8
Elongation set, %, after 200% prestrain			
after 15 min	14	11	90
after 1 hr	6	4	20
Resilience, %	33	35	26
Abrasion, % of ref.	87	83	131



this test can be concluded from a comparison between the properties of the unaged powder and the results of a test series carried out at 25°C/28 days. In spite of the long duration of the test the mechanical properties had only slightly changed, and the powders remained pourable.

The aging resistance of the powders can be considerably improved by the addition of suitable antioxidants. Among many types tested, those based on special phenylenediamines and phenols proved most effective (details of examples are given in Table VII). For optimum distribution of the antioxidant, water dispersions must first be prepared. The preparation of stable emulsions offers some problems, and the optimum formulations depend strongly on the type of antioxidant. An example is the composition of an emulsion provided with antioxidant 4010 NA: 40 g 4010 NA, 1 g Vanisperse CB, 5 g 5% casein solution, and 40 g water. This emulsion has a solids content of 46.5%.

The powder preparation was carried out as described above so that the final powder composition was as follows: 70 g polymer, 30 g Corax 4, 5 g Aerosil R 972, and 0.7 g antioxidant.

An example for the effectiveness the result of an aging test with NR and SBR masterbatch powders (compound formulation in Table VIII) is given in Table IX. It can be seen that the whole level of mechanical properties is only slightly influenced by the aging test so that the powders can be regarded as sufficiently protected against oxidative influences under similar time/temperature conditions.

### CONCLUSIONS

The preparation of rubber powders according to the above described method is characterized by its outstanding simplicity; indeed, it is difficult to imagine a simpler one. The above findings were obtained by the use of normal laboratory

TABLE VII  
Details of Effective Antioxidants Applied for Aging Protection

Phenol Type
2,2'-Methylenebis(4-methyl-6- <i>tert</i> -butylphenol) Antioxidant 2246 (Nordmann and Rassmann)
Phenylenediamine Type
N-isopropyl-N'-phenyl- <i>p</i> -phenylenediamine Vulkanox 4010 NA (Bayer AG)
N,N'-Di- $\beta$ -naphthyl- <i>p</i> -phenylenediamine Anchor DNPD (Anchor Chemicals)

TABLE VIII  
Formulations of Compounds Used for Aging Tests

	NR compound	SBR compound
NR powder, masterbatch	150	—
SBR powder, masterbatch	—	150
Zinc oxide	5	4
Stearic acid	3	2
Naftolen ZD	3	8
Sulfur	2.5	1.75
Vulkacit CZ	0.5	—
Flektol flakes	0.5	0.5
Light-protecting wax G 35	0.5	0.5
Cure: 143°C/20 min		
Milling at 70°C		

TABLE IX  
Effectiveness of Antioxidants with Rubber Powder Aging (70°C/7 Days)<sup>a</sup>

	Anchor DNPP		Antioxidant 2246	
	u	a	u	a
SBR Compound				
Hardness, Shore A	60	62	64	66
Tensile strength, MN/m <sup>2</sup>	25.5	26.0	27.8	26.9
Elongation at break, %	750	710	670	630
Modulus, NM <sup>2</sup>				
50%	1.1	1.2	1.3	1.4
100%	1.7	1.9	2.2	2.3
200%	3.5	4.0	4.9	5.4
300%	6.0	7.0	8.5	9.3
Tear strength, kN/m	25.5	27.2	26.9	26.5
Elongation set, %, after 200% prestrain				
after 15 min	16	16	20	16
after 1 hr	6	6	6	6
Resilience, %	32	31	29	30
NR Compound				
	Anchor DNPD		Vulkanox 4010 NA	
	u	a	u	a
Hardness, Shore A	62	65	61	61
Tensile strength, MN/m <sup>2</sup>	32.0	30.9	31.6	30.1
Elongation at break, %	550	580	570	560
Modulus, MN/m <sup>2</sup>				
50%	1.5	1.4	1.5	1.5
100%	2.8	2.4	2.4	2.6
200%	6.5	5.7	5.5	6.2
300%	12.6	11.1	10.9	11.3
Tear strength, kN/m	44.2	49.1	38.6	42.7
Elongation set, % after 200% prestrain				
after 15 min	11	11	9	10
after 1 hr	7	6	6	6
Resilience, %	44	40	45	42

<sup>a</sup> u: Unaged powder; a: aged powder.

equipment, and no optimization with respect to economy and product quality was attempted, which besides would depend on the respective latex/filler type.

It is thought that the engineering know-how of a continuous procedure would not be difficult to establish. On the other hand, the power consumption necessary for water evaporation during drying should be borne in mind. It is felt that the further development of the dry latex process will depend on the balance between its technical simplicity and its energy demand.

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