

# Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. VII. Treatment of Copolymer after Polymerization

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## Synopsis

The various procedures for removing the residual reactants and impurities from the polymer particle obtained by the solid-state copolymerization of tetraoxane with 1,3-dioxolane have been examined. The removal of the residual reactants by washing with solvents, such as acetone or water, were very difficult, because the residual reactants are mainly located in the central part of the polymerized particle. By evacuation of the polymeric system just after polymerization, however, the residual reactants were found to be easily eliminated from the polymer particle. It was also found that the polymer degradation caused by the acid impurities formed during polymerization can be prevented satisfactorily by neutralization using gaseous ammonia. On the basis of these findings, the simple process for polyoxymethylene production has been achieved; i.e., it was found that the polymer particle including the residual reactants and impurities can be directly pelletized using a vent-type extruder, immediately after the copolymerization procedure and the ammonia gas treatment, to obtain the polyoxymethylene pellet with an excellent thermal stability and a well controlled molecular weight.

## INTRODUCTION

As reported previously,<sup>1,2</sup> oxymethylene copolymer with an excellent thermal stability can be easily obtained in a high yield by the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane. In this copolymerization system, the molecular weight of the copolymer was found to be easily controlled by methylal. From the standpoint of technical production of oxymethylene copolymer, this copolymerization system can be expected to be one of the most promising processes, for the reactor for this copolymerization is very compact, as compared with those in a liquid-state copolymerization system, since a solvent is unnecessary.

However, in the solid-state copolymerization of tetraoxane with 1,3-dioxolane, the reaction proceeds from the surface to the center of monomer particle, so that unreacted tetraoxane remains mostly in the central part of the polymer particle obtained. It is difficult to remove the unreacted monomers and residual initiator from the copolymer particle. The particle as polymerized contains essentially a few percent of thermally unstable polymer, residual iodine, and acid impurities formed during the copolymerization reaction.

Since, as it is well known that oxymethylene polymer is easily decomposed by heating, alkalis, and acids to form formaldehyde, these impurities in the particle obtained by the copolymerization of tetraoxane would decompose the

copolymer to a lower thermal stability and molecular weight of the copolymer. In general, in order to pelletize an oxymethylene copolymer, it is necessary to obtain a copolymer having a thermal stability above 99% (the percentage of the residual weight after 60-min heating at 222°C under a stream of nitrogen) because small bubbles appear in a pellet when a copolymer having a thermal stability less than 99% is pelletized.

In this paper, we discuss post-treatment processes, such as neutralization of acid impurities contained in the copolymerization system, washing, and drying of the polymer particle obtained in this system. We also discuss the possibility of a simplified polymerization process in which no solvent is used in the entire process from polymerization to pelletization.

## EXPERIMENTAL

### Materials

Purifications of tetraoxane, 1,3-dioxolane, methylal, and iodine were described in a previous paper.<sup>1</sup> Methanol, acetone, ammonia gas, and sodium thiosulfate were obtained commercially and were used without purification. The commercial oxymethylene copolymer, Duracon M 90, obtained from Polyplastics Co. Ltd., was used.

### Polymerization

Although the various copolymerization methods were previously examined in detail,<sup>2</sup> only the continuous addition copolymerization was adopted for this work. The copolymerizations except for the cases in Table VII were done under the following conditions: 1,3-dioxolane, 3.5%; methylal, 0.18%; iodine, 30 ppm; copolymerization for 60 min at 107°C. (The concentrations of 1,3-dioxolane and methylal were calculated by percentage of milliliter per gram of tetraoxane and denoted in an abbreviated form by %. Iodine was denoted by ppm based on the amount of tetraoxane.) The copolymerization condition in Table VII was 1,3-dioxolane, 5.0%; methylal, 0.18%; iodine, 30 ppm; copolymerization for 60 min at 107°C. The addition methods of 1,3-dioxolane and methylal were described in a previous paper.<sup>2</sup>

### Washing

In order to remove the residual reactants and impurities from the copolymer, the polymerized particle was washed in the following three ways ("polymerized" particle was obtained just after the copolymerization procedure and not subjected to any other treatments; i.e., it consists of copolymer, residual monomers, and iodine, and impurities formed during polymerization):

1. The polymerized particle was washed with methanol by 5 times its weight at room temperature and 50°C. Methanol was replaced at 30-min intervals, and the amounts of tetraoxane dissolved in methanol were measured by gas chromatography.

2. To compare the solvents for washing, the polymerized particle was washed with various solvents for 60 min at room temperature. The solvents were re-

newed at 30-min intervals. The polymer particle washed was filtered and dried, and then the thermal stability of the copolymer was measured. (The "polymer" particle was obtained after removing the residual reactants and impurities.)

3. The polymerized particle was immersed in a large excess of the water-acetone solution (1:1 by volume) containing 2-wt. % sodium thiosulfate to neutralize the iodine and other impurities which may be formed during polymerization. Subsequently, the particle filtered was washed several times with excess water at room temperature, and then washed with hot acetone for 10 min. Finally, the copolymer was filtered and dried *in vacuo* until a constant weight was reached.

Unless otherwise indicated, the polymerized particle was washed exactly according to the washing procedure 3.

### Removal of Residual Reactant by Evacuation

In order to remove the residual reactants without use of any solvents, the polymerization reactor was evacuated by using a vacuum pump (Hitachi Ltd., Model 3VP-C) after copolymerization. The evacuation was carried out for 30 min at a reduced pressure of less than 50 Torr. During the evacuation the reactant in the reactor was kept at the copolymerization temperature (107°C).

### Ammonia Gas Treatment

Immediately after copolymerization, the polymerized particle was put into a container and contacted with ammonia gas for 10–15 min at room temperature. The pressure of ammonia gas was kept at 1 kg/cm<sup>2</sup>.

### Pelletizing of Copolymer

The polymer particle was mixed with 0.6 wt. % Yoshinox BB (Yoshitomi Pharmaceutical Co. Ltd.) and 1.0 wt. % Amilan CM-4000 (Toray Co. Ltd.) as an antioxydant and a formaldehyde scavenger, respectively, by using a Henshell Mixer (Mitsumiike Seisakusho Co. Ltd., Model FM-20B). The Henshell Mixer was operated for 15 min at 3000 rpm. The mixed powder thus obtained was pelletized with a vent-type extruder (Tanabe Plastics Machine Co. Ltd., Model VE-40-26). The operating conditions are listed in Figure 1.

### Sampling and Measurements of Thermal Stability, Intrinsic Viscosity, and Yield

The polymer particle samples used for the measurements of the intrinsic viscosity and the thermal stability of the copolymer were obtained by repeating

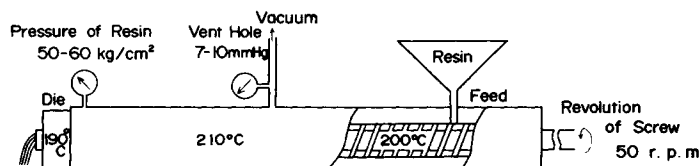


Fig. 1. Schematic drawing of extruder and its operation condition.

conical quartering, and were ground into fine powder except when determining the effects of polymer particle size on these copolymer properties. In the latter case, the polymer particle samples were classified according to their particle size as follows: (a) under 120 mesh (smaller than 0.125 mm), (b) 120–70 mesh (0.125–0.210 mm), (c) 70–30 mesh (0.210–0.595 mm), (d) 30–18 mesh (0.595–1.000 mm), and (e) over 18 mesh (larger than 1.000 mm). The pellet sample was ground into powder by using a cutter mill when its thermal stability and intrinsic viscosity were measured.

The copolymer yield was determined gravimetrically. The solution viscosity of the copolymer was measured at 60°C in *p*-chlorophenol containing 2%  $\alpha$ -pinene after the polymer sample was dissolved at 115°C within 15 min. The molecular weight of the sample was calculated using the equation<sup>3</sup>

$$[\eta] = 5.43 \times 10^{-4} \bar{M}_n^{0.66}$$

The thermal stability of the copolymer was determined by the weight-loss measurement under a stream of nitrogen gas at 222°C using a thermobalance, and it was quoted as the  $R_{222}^{60}$  value, i.e., the percentage of the residual weight after 60 min heating at 222°C.

### pH Measurement

The polymerized particle sampled at an appropriate time was immediately immersed in distilled water and allowed to stand overnight at room temperature. An acidity of the solution thus obtained was measured by using a pH meter (Mitamura Riken Co. Ltd., Model 10-255V).

## RESULTS AND DISCUSSION

In order to evaluate the solid-state copolymerization from the viewpoint of industrial application, the removal of the residual reactants and impurities contained in the polymer particle is very important. The various methods to remove them from the polymerized particle were examined. The residual tetraoxane in the polymerized particle was extracted with methanol and measured by gas chromatography. The extraction was repeated 5–6 times by using fresh methanol. These results are shown in Table I. It was found that the amount

TABLE I  
Tetraoxane<sup>a</sup> Extracted by Washing with Methanol

Repetition <sup>b</sup>	Room temperature			50°C	
	under 120	70 ~ 30	over 18	70 ~ 30	over 18
1	$6.12 \times 10^{-2}$	$3.14 \times 10^{-2}$	$2.45 \times 10^{-2}$	$3.76 \times 10^{-2}$	$3.05 \times 10^{-2}$
2	$1.36 \times 10^{-2}$	$6.43 \times 10^{-3}$	$6.45 \times 10^{-3}$	$8.51 \times 10^{-3}$	$7.21 \times 10^{-3}$
3	$3.01 \times 10^{-3}$	$2.22 \times 10^{-3}$	$3.08 \times 10^{-3}$	$2.05 \times 10^{-3}$	$2.01 \times 10^{-3}$
4	$6.6 \times 10^{-4}$	$7.4 \times 10^{-4}$	$1.76 \times 10^{-3}$	trace	$1.05 \times 10^{-3}$
5	trace	trace	$1.02 \times 10^{-3}$	trace	$4.9 \times 10^{-4}$
6	trace	trace	$5.8 \times 10^{-4}$	trace	trace
Total amount of extracted tetraoxane	$7.85 \times 10^{-2}$	$4.35 \times 10^{-2}$	$3.74 \times 10^{-2}$	$4.82 \times 10^{-2}$	$4.13 \times 10^{-2}$

<sup>a</sup> Tetraoxane (g/g) based on polymerized particle.

<sup>b</sup> Methanol was renewed at 30-min intervals.

of extracted tetraoxane increased with decreasing particle size and with increasing extraction temperature. The number of repetitions at which the amount of extracted tetraoxane becomes trace was also found to decrease as particle size decreases and extract temperature increases. It is very doubtful whether the residual tetraoxane can be thoroughly removed from the polymerized particle only by washing with solvent. So the polymerized particle washed with the water-acetone solution containing 2 wt. % sodium thiosulfate was mechanically crushed into a fine powder using a roll mill. The fine powder thus obtained was washed again with the water-acetone solution containing 2 wt. % sodium thiosulfate, and then the recovery and thermal stability of the powdery copolymer after washing were measured as shown in Table II. When the particle size is less than 30 mesh, the recoveries of the powdery copolymer were nearly equal to 100% and their thermal stabilities scarcely changed before and after crushing and washing. However, at a particle size larger than 30 mesh, the recovery was less than 100% and their thermal stabilities became slightly higher by crushing and washing.

The degradation of the copolymer obtained in this copolymerization system was investigated. Immediately after copolymerization, the polymerized particles, including the residual monomers and impurities formed during copolymerization, were allowed to stand in contact with air at room temperature or 100°C. Table III shows the effects of standing time and temperature on the thermal stability and molecular weight (intrinsic viscosity) of the copolymer.

TABLE II  
Recovery and Thermal Stability of Copolymer Washed after Mechanical Crush

Particle size <sup>a</sup> of copolymer (mesh)	Before crushing	After crushing and washing	
	Thermal stability $R_{222}^{90}$ , %	Recovery <sup>b</sup> %	Thermal stability $R_{222}^{90}$ , %
under 120	97.5	99.9	97.5
120 ~ 70	97.9	100.0	97.7
70 ~ 30	97.8	99.9	97.5
30 ~ 18	95.6	99.7	96.3
over 18	93.8	99.6	96.7

<sup>a</sup> Copolymer particle was sieved after washing.

<sup>b</sup> This represents the recovery of powdery copolymer based on the weights before and after washing.

TABLE III  
Effects of Standing in Air on Yield, Thermal Stability, and Intrinsic Viscosity of Copolymer

Standing time hr	Particle size mesh	Room temperature (25°C)			100°C		
		Polymer yield %	Thermal stability $R_{222}^{90}$ , %	Intrinsic viscosity $[\eta]$ , dl/g	Polymer yield %	Thermal stability $R_{222}^{90}$ , %	Intrinsic viscosity $[\eta]$ , dl/g
0	under 70	89.3	97.2	1.5	89.3	97.2	1.5
0.5	under 70	90.0	95.0	1.3	92.9	97.2	1.5
1	under 70	90.3	95.1	1.3	94.2	97.3	1.5
2	under 70	90.8	95.4	1.2	95.4	96.5	1.4
4	under 70	91.2	95.1	1.3	96.0	94.7	1.2
18	under 70	91.8	95.0	1.2	98.2	70.7	0.9

In the case of room temperature, the thermal stability and intrinsic viscosity of the copolymer decreased rapidly within 30 min and then became nearly constant at a standing time greater than 30 min, while a change in the copolymer yield was scarcely observed at an entire range of standing time examined. Therefore, the decreases in the thermal stability and intrinsic viscosity of the copolymer during the first 30 min of standing time may be attributed not to the formation of the copolymer in standing time, but to the chain scissions due to the acid impurities formed during copolymerization. On the other hand, in the case of standing at 100°C, the thermal stability and intrinsic viscosity of the copolymer decreased monotonically with increasing standing time, and finally reached 70% and 0.9 dl/g at 18 hr, respectively. The copolymer yield was also found to increase with increasing standing time. Therefore, it is reasonably suggested that, when the polymerized particle was kept at 100°C in air, the copolymer having low thermal stability and low intrinsic viscosity is formed and the copolymer is gradually degraded by the mutual interaction of heat and impurities contained in the particle, because the thoroughly washed copolymer has an excellent thermal stability and is scarcely decomposed at 100°C.

It is known<sup>4</sup> that, in oxymethylene polymer, main chain scission occurs easily in the presence of acids and alkalis to lower molecular weight of the copolymer, and that an oxymethylene polymer with a hydroxyl end group decomposes even at 100°C. The acidity of this copolymerization system was examined as follows. The polymerized particle was sampled out from the reactor at appropriate time intervals and immersed into distilled water to extract acids formed during copolymerization. The acidity of the extract thus obtained was measured by using a pH meter as shown in Table IV. The acidity of the polymerized particle was found to increase as the copolymerization proceeded. This fact indicates that some acid impurities accumulate in the polymerized particle. In this copolymerization system, two different acid impurities may be formed: one is the formic acid which is formed by oxidation of formaldehyde, the other the acid impurities which may be formed by reaction between iodine and oxygen or water. Ishigaki et al.<sup>5</sup> reported that, in the radiation-induced post-polymerization of trioxane in the solid state, main chain scission of polyoxymethylene is caused by formic acid formed during polymerization. Therefore, in order to obtain an oxymethylene copolymer having an excellent thermal stability and a higher molecular weight in the copolymerization of tetraoxane, the acid impurities in the polymerized particle should be neutralized immediately after copolymerization. Figure 2 shows thermal stability of the copolymer washed with various

TABLE IV  
pH of the Extract<sup>a</sup>

Polymerization time, min	pH value
2	6.38
12	6.39
22	6.25
35	6.21
45	6.19
60	6.00

<sup>a</sup> The water solution extracted acids from the polymerized particle.

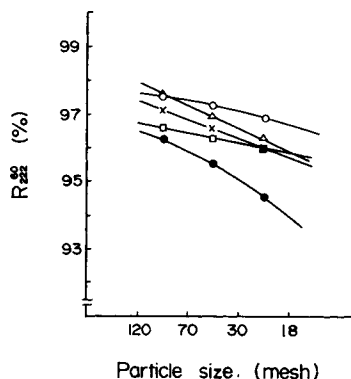


Fig. 2. Thermal stability of copolymer after washing with various solvents: (O), water-acetone solution containing 2 wt. % sodium thiosulfate; ( $\Delta$ ), 4 mol% aqueous ammonia solution; (X), water; ( $\square$ ), methanol; ( $\bullet$ ), acetone.

solvents. The polymer particles were sieved and divided into four groups according to particle size after washing and drying. The thermal stabilities of the copolymer washed with aqueous ammonia solution or the water-acetone solution containing 2 wt. % sodium thiosulfate were higher than those of the copolymer washed with the solvent which does not contain any basic compounds. In the case of washing with the water-acetone solution containing 2 wt. % sodium thiosulfate, acetone causes the surface tension of the solution to diminish and makes the solution penetrate easily into the polymerized particle.

The results in Figure 2 indicate that it may be difficult for the solvent to penetrate thoroughly into the center of the polymerized particle, if the size of the particle is larger.

If the acid impurities and the residual monomers can be easily removed from the polymerized particles without any solvent, the process will become one of the most promising methods for polyoxymethylene production. The authors tried to neutralize the acid impurities contained in the polymerized particle using gaseous ammonia and to evacuate the residual monomers from the polymerized particle under reduced pressure. The polymerized particles were exposed to gaseous ammonia for 10–15 min immediately after they were sampled out from the reactor, and then washed with the water-acetone solution containing 2 wt. % sodium thiosulfate. The thermal stability and intrinsic viscosity of the copolymer thus obtained are shown in Table V as compared with those of the co-

TABLE V  
Effects of Ammonia Treatment of Thermal Stability and Intrinsic Viscosity of Copolymer

Particle size mesh	Ammonia treatment			Without ammonia treatment		
	Thermal stability $R_{222}^{60}$ , %	Intrinsic viscosity $[\eta]$ , dl/g	Polymer yield %	Thermal stability $R_{222}^{60}$ , %	Intrinsic viscosity $[\eta]$ , dl/g	Polymer yield %
under 120	99.1	1.6	—	98.3	1.5	—
70 ~ 30	99.3	1.7	—	98.4	1.6	—
30 ~ 18	99.1	1.8	—	97.9	1.7	—
Average <sup>a</sup> value	99.3	1.7	93.7	98.6	1.6	94.3

<sup>a</sup> Average value means the value of polymer sample obtained by repeating conical quartering.

polymer washed only with the water–acetone solution containing 2 wt. % sodium thiosulfate. The thermal stabilities of the copolymer were above 99%, and higher than those of the copolymer treated without gaseous ammonia. From these facts, it is surmised that gaseous ammonia diffuses more easily to a central part of the polymerized particle and neutralizes sufficiently the acid impurities in the polymerized particle. Therefore, the thermal stability of the copolymer retains a high value above 99%. The thermal stabilities of the copolymer exposed to gaseous ammonia were almost constant irrespective of the polymerized particle size, while those of the copolymer treated without gaseous ammonia decreased with increasing particle size. This fact may be explained by the difference in the penetration rates of gaseous ammonia and solution into the polymerized particle.

Further, after neutralization of the polymerized particle, we tried to remove the residual reactants from the polymerized particle without solvents. Both tetraoxane and iodine are sublimative. It has been shown that 1,3-dioxolane and methylal diffuse to a central part of the polymerized particle during the copolymerization reaction.<sup>6</sup> By using these characteristics, the residual monomers and iodine can be removed from the polymerized particle under the reduced pressure. Immediately after the copolymerization procedure, the copolymerization system was evacuated under a pressure less than 50 Torr at 107°C. Table VI shows the relationships between the polymer content, thermal stability, and intrinsic viscosity of the copolymer and the evacuation time. The vapor pressure of tetraoxane is 3.2 Torr at 40°C and 93 Torr at 112°C (112°C is the melting point of tetraoxane at atmospheric pressure). When the polymerized particle was kept under reduced pressure for 30 min, the copolymer content and thermal stability were found to rise from 91.4 and 97.4% to 99.4 and 98.8%, respectively. No change in the intrinsic viscosity of the copolymer was recognized before and after evacuation. On the other hand, the polymerized particles evacuated under reduced pressure were washed with the water–acetone solution containing 2 wt. % sodium thiosulfate and then crushed mechanically to fine powder using a roll mill. The recovery of the copolymer was 100% after the fine powder was washed again with the water–acetone solution containing 2 wt. % sodium thiosulfate. There are no differences in the thermal stability and intrinsic viscosity of the copolymer for the fine powder and for the original particle which was not crushed and not washed after evacuation. Consequently, it is concluded that the residual tetraoxane and iodine can be almost completely removed by evacuation immediately after copolymerization.

As mentioned above, this copolymerization can be characterized as follows: (1) the oxymethylene copolymer with an excellent thermal stability can be easily obtained in a high polymer yield; (2) the acid impurities formed during poly-

TABLE VI  
Effects of Evacuation on Yield, Thermal Stability, and Intrinsic Viscosity of Copolymer

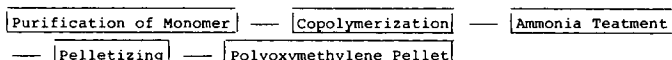
	Evacuation time, min				
	0 <sup>a</sup>	5	10	20	30
Polymer content, %	91.4	95.1	97.0	98.4	99.4
Thermal stability $R_{222}^{60}$ , %	97.4	98.5	98.7	98.7	98.8
Intrinsic viscosity $[\eta]$ , dl/g	1.4	1.5	1.4	1.5	1.5

<sup>a</sup> Immediately after the copolymerization.



merization can be neutralized using gaseous ammonia; (3) the residual monomers and iodine can be removed from the polymerized particles by evacuation of the polymeric system. Based on these characteristics, the authors tried to simplify the processes for production of oxymethylene copolymer, i.e., to omit the processes of washing and drying of the copolymer. The polymerized particles, which were obtained by the process of polymerization and which contained the residual monomers and acid impurities, were neutralized by contact with gaseous ammonia and then pelletized by using a vent-type extruder. The thermal stability and intrinsic viscosity of the oxymethylene copolymer pellet thus obtained are listed in Table VII in comparison with those of the pellet obtained after washing and drying. It can be seen that the residual monomers and impurities contained in the polymerized particle can be evaporated and easily removed by evacuation during the process of pelletization, because the thermal stability of the pellet obtained by this simplified process is nearly equal to that of the pellet produced via the processes of washing and drying, and to that of the commercial oxymethylene copolymer, Duracon M 90. Consequently, it was found that the processes of washing and drying in the processes for production of an oxymethylene copolymer can be omitted by the gaseous ammonia treatment and by evacuation during the process of pelletization. Figure 3 shows two different block diagrams of the processes for the manufacture of oxymethylene copolymer; (A) is the process for the solid-state copolymerization of tetraoxane with 1,3-dioxolane and (B) is the process for the liquid-state copolymerization of trioxane with ethylene oxide which is presumed from a U.S. Patent<sup>7</sup> registered by Celanese Co. Ltd. The former is very simple as compared with the latter, and has the advantage of minimizing the plants, because no solvent is used in the processes.

Process A; Solid-state Copolymerization of Tetraoxane with 1,3-Dioxolane



Process B ; Liquid-state Copolymerization of Trioxane with Ethylene Oxide

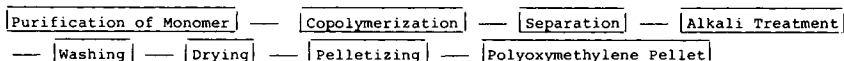


Fig. 3. Block diagrams of process for manufacture of oxymethylene copolymer. Process B was presumed by U.S. Patent<sup>7</sup> registered by Celanese Co., Ltd.

TABLE VII  
Thermal Stabilities of Copolymers before and after Pelletization

	Direct pelletization <sup>a</sup>		Pelletization <sup>b</sup>		Duracon M 90 pellet
	Before <sup>c</sup>	After	Before	After	
Thermal stability $R_{222}^{60}$ , %	94.2	99.85	99.4	99.8	99.4
Intrinsic viscosity $[\eta]$ , dl/g	-	1.4	1.4	1.5	1.4

<sup>a</sup> Copolymer was treated with gaseous ammonia after the copolymerization.

<sup>b</sup> Copolymer was washed and dried after the copolymerization and crushed into fine powder and then washed and dried again.

<sup>c</sup> This particle contains residual monomers, other reactants and impurities.

The authors would like to thank M. Yokooji, K. Uemura of Ube Industries, Ltd., Dr. A. Shimizu of Mitsubishi Yuka Co. Ltd., and Y. Fujita of Mitsuitoatsu Co. Ltd., for carrying out the experiments, the helpful discussions and suggestions.

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