INTERIM REPORT

SUSPENSION POLYMERIZATION OF VINYL CHLORIDE:

RATES OF POLYMERIZATION WITH MIXTURES OF DILAUROYL PEROXIDE AND DIISOPROPYL PEROXYDICARBONATE

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SUMMARY A significant reduction in the time required for the suspension polymerization of vinyl chloride could be achieved if an initiator system could be developed to give a constant rate of polymerization. Suspension polymerizations of vinyl chloride were conducted in glass bombs with mixtures of the two initiators, dilauroyl peroxide and diisopropyl peroxydicarbonate, to determine if some combination of the two might help to overcome the autocatalytic nature of the polymerization.

Several combinations of the two initiators were evaluated. Each successive increase in the initial rate of polymerization was accompanied by an increase in the maximum rate of polymerization. Some changes in the rate-conversion relationship were observed, but further work will be required to determine if the indicated improvement in rate is real or is the result of the experimental error. The hypothesis was advanced that an initiator with a shorter half-life than diisopropyl peroxydicarbonate will be required to achieve a constant rate throughout the polymerization.

Combinations of dilauroyl peroxide with peracetic acid and with dimethylaniline were also evaluated. The peracetic acid decreased the initial rate of polymerization while the dimethylaniline gave reduced rates over the entire period during which the reaction was followed.

DISCUSSION

Mixtures of Diisopropyl Peroxydicarbonate and Dilauroyl Peroxid

The suspension polymerization of vinyl chloride at 50°C, when initiated with 0.30 weight per cent of dilauroyl peroxide (DLP), has been shown to have an initial rate of polymerization of 2.5 and a maximum rate of 11.2 per cent

conversion per hour (1). The time required for 90 per cent conversion in this system is 13 hours. If a constant rate of polymerization of 11.2 per cent could be achieved, then the time to 90 per cent conversion would be reduced to 8 hours, a reduction of 38 per cent*. It has been postulated by the Texas City Development Group that the use of a small amount of a very active initiator in combination with DLP might help to achieve a more uniform rate of polymerization. The relatively high order of activity of diisopropyl peroxydicarbonate (IPP) suggested that this material should be evaluated in combination with DLP.

Suspension polymerizations of vinyl chloride were conducted in glass bombs at 50°C, and conversion-time curves were obtained for the following initiator combinations:

1. 0.047 mol per cent IPP**
2. 0.035 mol per cent IPP plus 0.012 mol per cent DLP
3. 0.0235 mol per cent IPP plus 0.0235 mol per cent DLP
4. 0.012 mol per cent IPP plus 0.035 mol per cent DLP
5. 0.004 mol per cent IPP plus 0.047 mol per cent DLP
6. 0.047 mol per cent DLP

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* The heat transfer capacity of production autoclaves necessitates the use of a polymerization period of around 21 hours. Under these conditions the initial rate is probably close to 1 per cent and the maximum rate close to 8 per cent conversion per hour. A constant rate of 8 per cent per hour would reduce the time required for 90 per cent conversion to 11.2 hours, a reduction of 47 per cent.

** The weight percentages are related to the mol percentages by the equation:

$$\text{Wt. per cent} = \frac{\text{Mol. wt. of Init.}}{\text{Mol. wt. of VCl}} \times [\text{Mol per cent}]$$

These molecular weight ratios are 6.38 and 3.30 for dilauroyl peroxide and diisopropyl peroxydicarbonate, respectively.

The conversion-time curves for these systems are plotted in Figure 1 and are the best continuous curves that could be drawn through the experimental data. The rates of polymerization at increments of 10 per cent conversion were calculated from the conversion curves by use of the equation:

$$\text{Rate} = \frac{f(t+\Delta)-f(t-\Delta)}{(t+\Delta)-(t-\Delta)},$$

where $f(t+\Delta)$ is the degree of polymerization at the time $(t+\Delta)$, etc. The values of t used were the times required to reach the degree of conversion at which the rate was desired, and a value of 1/8 hour was used for Δ. The calculated rates are given in Table II and are plotted in Figure 2.

The results in Table II show that each successive increase in the initial rate results in an increase in the maximum rate. The simple procedure of adding some IPP to a system containing the normal amount of DLP did not help to improve the constancy of the rate. Thus, the system number 5 was constant to the extent of 12.4 ± 2 per cent from 30 per cent to 80 per cent conversion, and system number 6, without any IPP, was constant to the extent of 9.2 ± 2 per cent from 30 to 80 per cent also. Perhaps some lower total concentration of the two peroxides or a different ratio might improve this picture.

A system which did show a constant rate over a longer range of conversions was 0.012 mol per cent of IPP alone at 50°C. This system was the lowest concentration of IPP for which rates from 0 to 90 per cent conversion could be calculated. The measurements on this system were made as part of a previous study (2). The calculated rates for this system were:

TABLE I

System #7

Conversion, Per Cent	Rate of Polymerization, Per Cent Conversion per Hour
0	5.0
10	9.4
20	13.4
30	13.0
40	14.0
50	14.8
60	15.0
70	15.6
80	16.2
90	12.4

This system had a constant rate to the extent of 14.2±2 per cent from 20 to 90 per cent conversion. The results for this system are also plotted in Figure 2.

The rate versus conversion curves plotted in Figure 2 give some indication that the nature of the dependence on the degree of monomer conversion can be altered by the choic of initiator system; this is especially true of the results for system number 4. However, in view of the experimental errors involved in the use of IPP, it is considered more probable that the deviations in the shapes of the curves, including the results for systems 4 and 7, are the result of the experimental error. It is very difficult to charge the exact amounts of vinyl chloride and IPP to the bombs; a few of the "duplicate bombs" gave differenc s in conversion as high as eight per cent. Since none of the indicated improvements in rate are greater than the possible experimental error, more work will be required to determine if combinations of IPP and DLP can improve the rate and to determine the extent of the improvement.

The autocatalytic nature of the polymerization of vinyl chloride has been attributed to the reduction of the rate of termination and the resultant increase in free radical concentration (3). If a sufficiently reactive initiator could be found so that the concentration of initiator (and therefore the rate of formation of free radicals) would decrease in the same ratio as the rate of termination, then a constant rate of polymerization would be anticipated (with due allowance for the decrease in monomer concentration). The half-lives for DLP and IPP at 50°C are 50 hours and 6.8 hours, respectively (4). A peroxide with a shorter half-life than 6.8 hours is probably required to radically alter the rate-conversion behavior of the suspension polymerization of vinyl chloride.

Peracetic Acid or Dimethylaniline with Dilauroyl Peroxide

The effects of additions of peracetic acid and of dimethylaniline (DMA) on the conversion-time behavior were also determined. Conversion-time curves were obtained from 0 to 8 hours for suspension polymerizations at 50°C with the following initiator systems:

A. 0.047 mol per cent DLP
B. A plus 0.05 mol per cent peracetic acid
C. A plus 0.0047 mol per cent DMA
D. A plus 0.047 mol per cent DMA
E. A plus 0.41 mol per cent DMA

The results of these measurements are plotted in Figure 3. As can be seen in the figure, the peracetic acid lowered the rate for roughly the first hour compared to system A, but after one hour gave rates similar to A alone. The DMA, however, gave lowered rates throughout the eight hour period, with the degree of lowering directly proportional to the amount of DMA included in the system. Thus, neither peracetic acid or DMA seems capable of producing the desired uniform rate. In addition, the DMA gave the polyvinyl chloride a poor color.

PROCEDURE The usual charging techniques (5) were employed except when IPP was added to the bombs. When IPP was added, the modified procedure was used (2), whereby the IPP was added in vinyl chloride solution at -78.5°C. The recipe used was as follows:

Water	16.2 ml
Vinyl Chloride	12.0 g
E-88-H (2 per cent aqueous solution)	1.8 ml
Initiator	variable

A sufficient number of bombs were charged in each to allow a pair of bombs to be taken from the batch each hour or half-hour (depending upon the rate of polymerization), and the degree of polymerization determined by recovery of the solids in the bombs. The difficulty usually encountered in getting exactly 12.0 grams of vinyl chloride in each bonb was partially circumvented by pairing the bombs which were high in added vinyl chloride with bombs which were low in added vinyl chloride, e.g., a bomb containing 12.3 grams of vinyl chloride would be paired with a bomb containing 11.7 grams of vinyl chloride. The exact weights of vinyl chloride, however, were used in the calculating of the degrees of conversion.

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Attachments:

3 Figures
1 Table

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TABLE II

SUSPENSION POLYMERIZATION OF VINYL CHLORIDE AT 50°C

POLYMERIZATION RATES FOR MIXTURES OF IPP* AND DLP* INITIATORS

MONOMER CONVERSION, %	POLYMERIZATION RATE, PER CENT CONVERSION PER HOUR						
	1	2	3	4	5	6	7
0	16.8	15.2	10.8	6.8	4.0	2.5	5.0
10	21.2	20.0	16.4	12.8	6.6	4.4	9.4
20	28.0	24.0	20.4	17.2	8.6	6.3	13.4
30	34.4	27.2	26.4	20.8	10.4	7.7	13.0
40	40.0	28.4	30.0	22.0	11.4	8.7	14.0
50	45.2	35.6	33.2	24.4	12.0	9.6	14.8
60	50.0	41.2	36.6	24.4	13.0	10.3	15.0
70	54.8	46.8	37.6	24.0	14.4	10.8	15.6
80	56.0	51.2	44.0	23.2	13.6	11.2	16.2
90	48.0	46.4	24.4	19.4	9.0	5.0	12.4

* IPP = Diisopropyl Peroxydicarbonate
DLP = Dilauroyl Peroxide

INITIATOR CONCENTRATIONS*

INITITATOR SYSTEM	IPP		DLP		TOTAL INITIATOR	
	Mol %	Wt %	Mol %	Wt %	Mol %	Wt %
1	0.047	0.16	-	-	0.047	0.16
2	0.035	0.12	0.012	0.076	0.047	0.20
3	0.0235	0.078	0.0235	0.15	0.047	0.23
4	0.012	0.040	0.035	0.22	0.047	0.26
5	0.004	0.013	0.047	0.30	0.051	0.31
6	-	-	0.047	0.30	0.047	0.30
7	0.012	0.039	-	-	0.012	0.039

* Calculated as weight and mole per cent of the vinyl chloride

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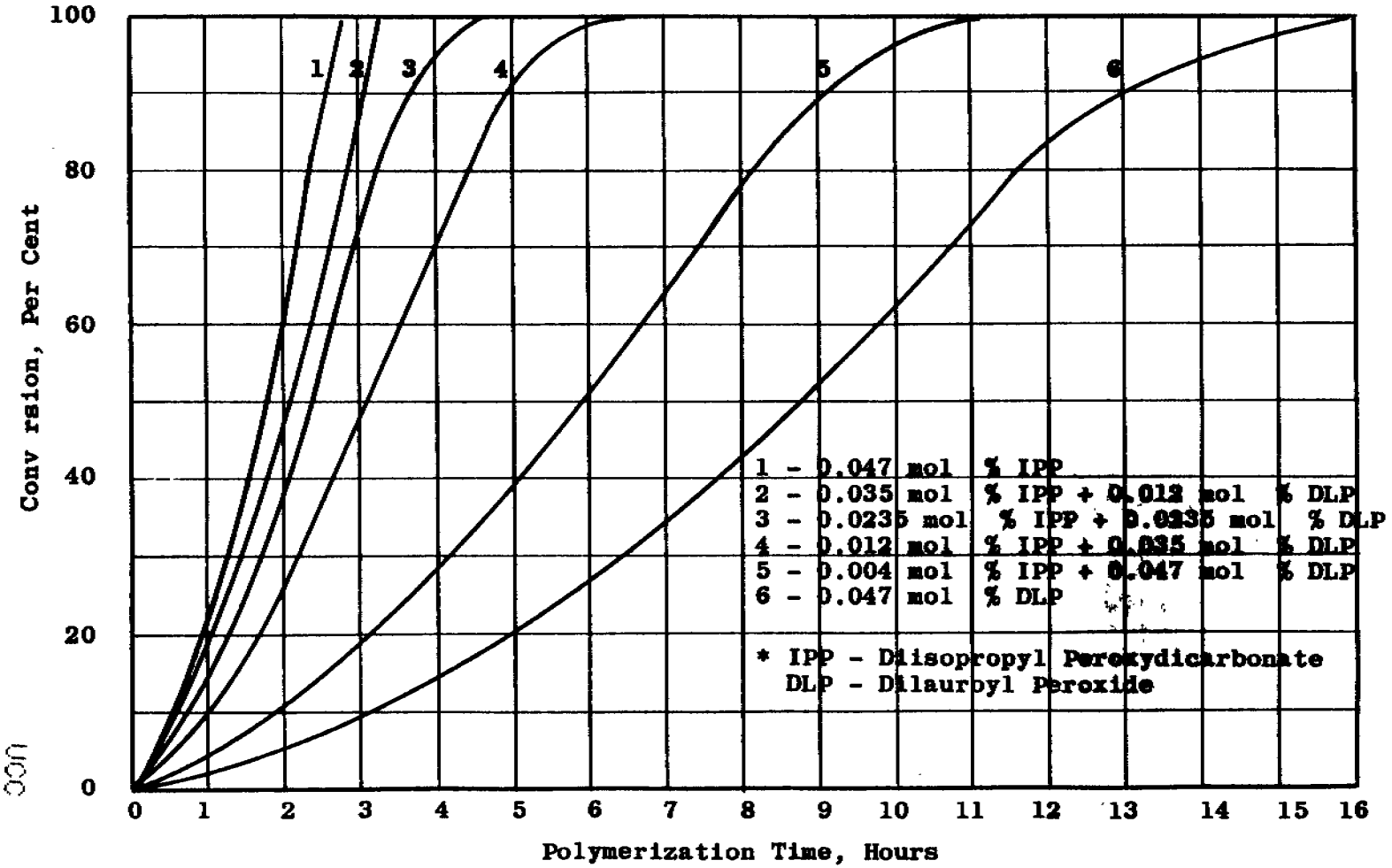
FIGURE 1

SUSPENSION POLYMERIZATION OF VINYL CHLORIDE AT 50°C:

CONVERSION CURVES FOR MIXTURES OF IPP* AND DLP* INITIATORS



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SUSPENSION POLYMERIZATION OF VINYL CHLORIDE AT 50°C
POLYMERIZATION RATES FOR MIXTURES OF IPP AND DLP INITIATORS

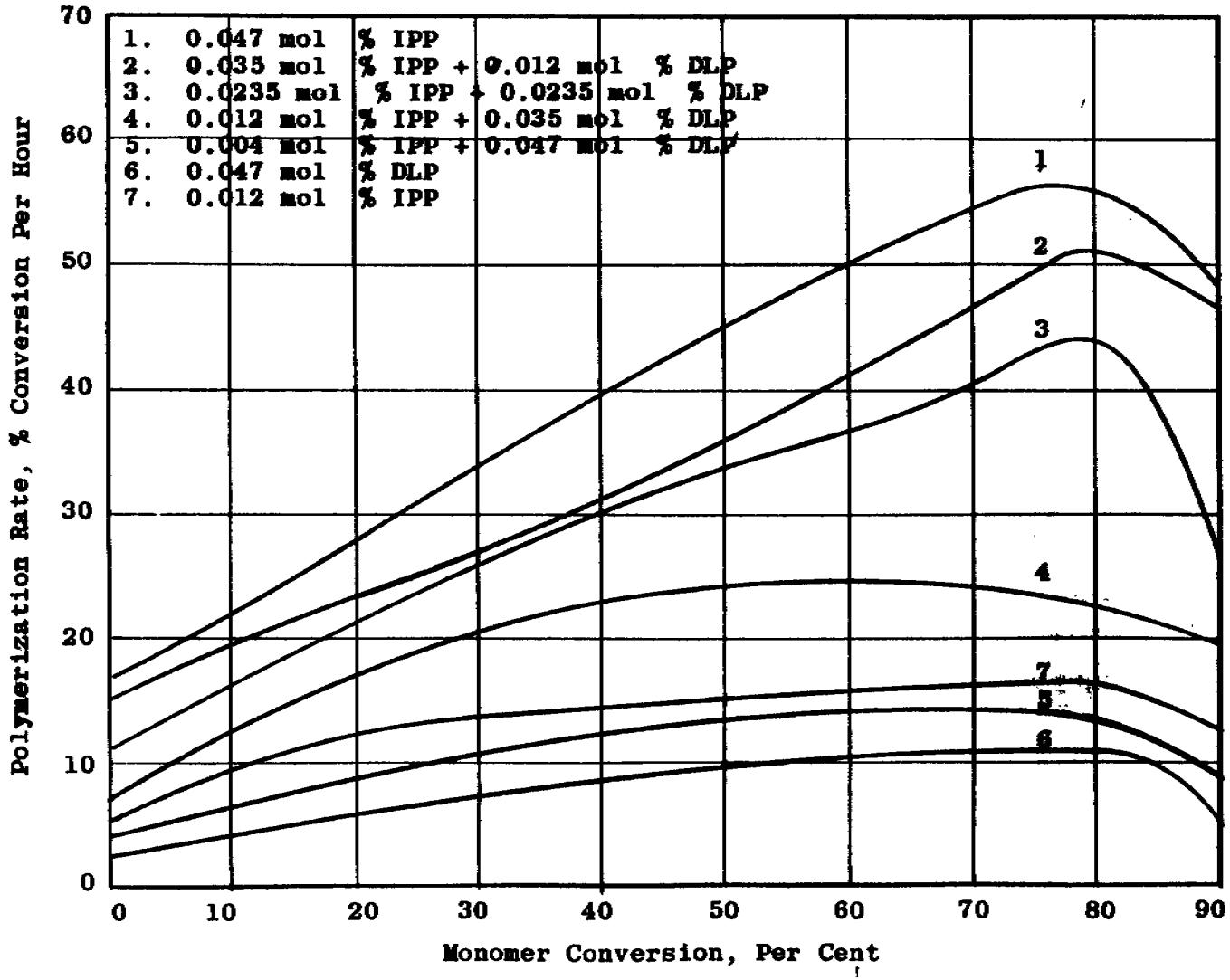

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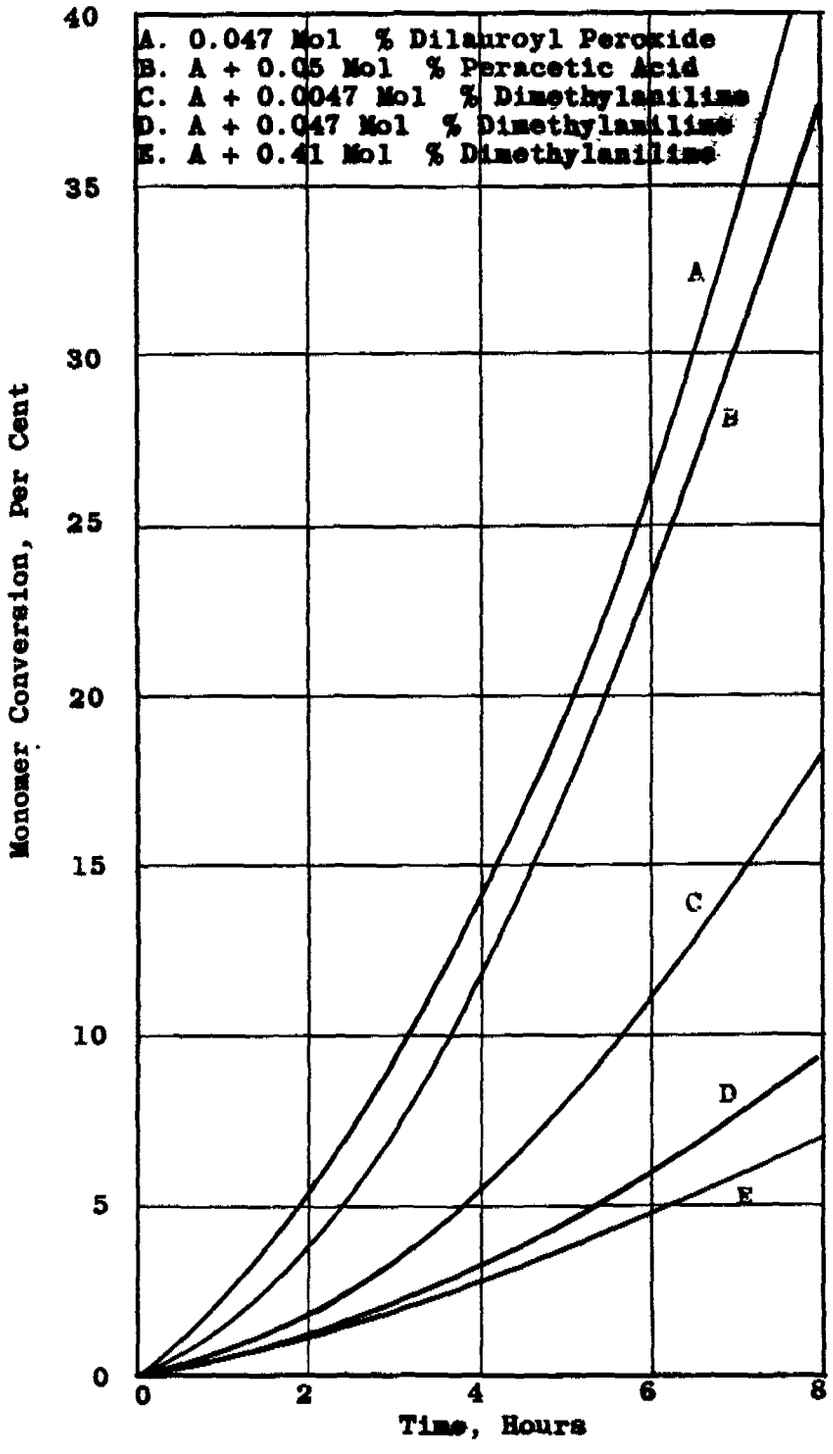
FIGURE 3

SUSPENSION POLYMERIZATION OF VINYL CHLORIDE AT 50°C:

EFFECTS OF PERACETIC ACID AND DIMETHYLANILINE ON CONVERSION



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