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Note

Application of the retention index system in the gas chromatographic analysis of industrial coke oven samples containing cyclopentadiene

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In a gas reforming plant, where coke oven gas is subjected to low-temperature fractional distillation using "cold boxes" to recover hydrogen, carbon monoxide and the hydrocarbon fractions, a problem often encountered is that of "line choking"¹. Presumably the accumulation of lower boiling hydrocarbons that escape recovery and are carried over with coke oven gas gives rise to solid deposits in the pipelines and causes a pressure drop in the system. This results in frequent shutdowns of the plant and necessitates deriming of the lines by washing out the deposits with a suitable solvent such as methanol.

This study was undertaken in order to obtain an insight into this problem of line choking by a systematic detailed analysis of the composition of derimed samples by a combination of gas chromatography and efficient fractional distillation.

EXPERIMENTAL

The components of the derimed samples were identified and determined by the method suggested by Mitra and co-workers²⁻⁴, which is particularly useful for the analysis of complex mixture of hydrocarbons of unknown nature in the absence of standard reference compounds.

Fractional distillation

The lines were derimed with a known amount of pure methanol. A 100-ml volume of the sample obtained was subjected to fractional distillation in a 120-plate column, maintaining a reflux ratio of 20:1. A Podbielniak Series-3475 Minical distillation apparatus was used for fractional distillation. The fractions collected are listed in Table I.

Gas chromatography

The gas chromatographic analyses of the composite derimed sample, the in-

TABLE I
FRACTIONS OBTAINED BY FRACTIONAL DISTILLATION OF DERIVED SAMPLES

Fraction	Boiling range ($^{\circ}\text{C}$)	Proportion (vol.%)
1	IBP-41	0.8
2a	41-55	16.1
2b	55-56	3.5
3	56-80	74.0
Residue	>80	5.3

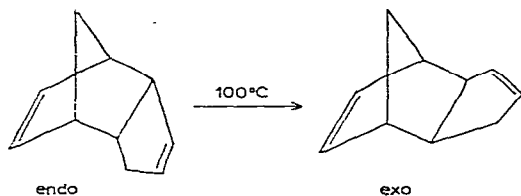
dividual fractions and the residue were carried out using a Varian Aerograph Model 600D chromatograph equipped with a flame-ionization detector. Two analytical columns (20 ft. \times 1/8 in. O.D.) packed with 5% SE-30 and 20% 1,2,3-triscyanoethoxypropane (TCEP) were employed at temperatures between 60° and 115° . The identification of the peaks and the interpretation of the chromatograms were carried out by comparing the retention behaviours of the components in the sample on these two stationary phases of opposite polarity. The retention indices (I) of peaks and shoulders, gas hold-up time, instrumental accuracy and column performances were determined in the conventional manner; the retention indices of the peaks are shown on the chromatograms.

RESULTS AND DISCUSSION

Standard samples

The dicyclopentadiene standard (supplied by E. Merck Darmstadt, G.F.R.) gave four and six peaks on a non-polar SE-30 and a polar TCEP column, respectively, indicating the presence of numerous components in the standard sample (Figs. 1 and 2). Dicyclopentadiene, with peak retention indices of 1046 on SE-30 and 1445 on TCEP, was the major constituent. Peaks with retention indices of 549 (SE-30) and 968 (TCEP) could be attributed to the monomer (*i.e.*, cyclopentadiene), the presence of which was confirmed by injecting a freshly cracked sample of dicyclopentadiene.

The other impurities in the sample appeared to be cyclodienes, as the ΔI values were each about 400 units. The peaks with a retention index of 960 on SE-30 possibly represented two components as it was resolved into peaks with retention indices of 1340 and 1370 on the TCEP column. Similarly, the peak with a retention index of 1046 on SE-30, which appeared as peaks with retention indices of 1398 and 1445 on TCEP, could tentatively be assigned to *exo* and *endo* isomers of dicyclopentadiene, respectively. Peaks with retention indices of 1105 on SE-30 and 1496 on TCEP could at best be attributed to some component with a structural resemblance to dicyclopentadiene.



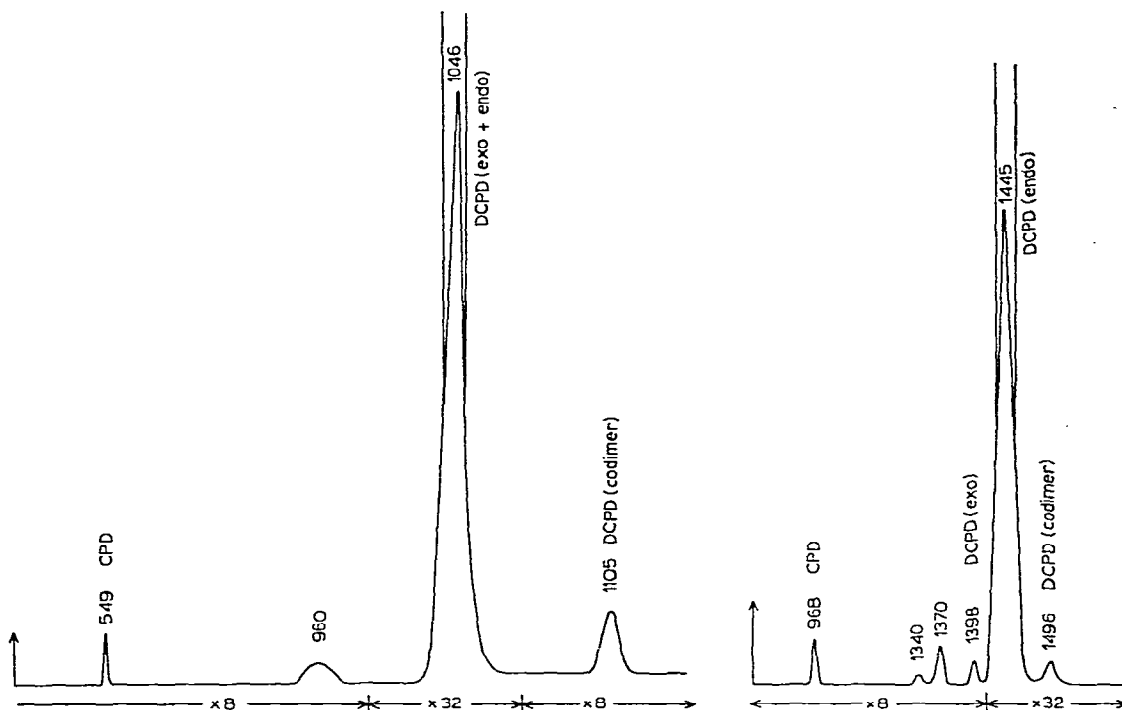


Fig. 1. Chromatogram of a standard sample of dicyclopentadiene on SE-30 at 115°. CPD, cyclopentadiene; DCPD, dicyclopentadiene.

Fig. 2. Chromatogram of a standard sample of dicyclopentadiene on TCEP at 115°. Compounds as in Fig. 1.

Derimed sample

In order to study the temperature coefficients of the retention indices (dI/dT), the freshly collected derimed sample was injected on to an SE-30 column at several temperatures under isothermal conditions. Chromatograms run at lower temperatures (*e.g.*, 40°) did not show components beyond retention index 700, possibly because the column temperature was not high enough. A more complete chromatogram on SE-30 obtained at 100° is presented in Fig. 3, which shows that the retention indices ranged from 272 to 1028, indicative of the presence of C₂-C₁₀ hydrocarbons. The absence of peaks with retention indices between 756 and 1028 was unusual because this would mean that C₈ and C₉ hydrocarbons were not present in the sample. In order to obtain more reliable information on peak identity with particular reference to molecular structure, a polar TCEP column was employed. Fig. 4 represents a typical chromatogram run at 100°. The various values of ΔI obtained by comparing the peak retention indices (in Figs. 3 and 4) ranged between 164 and 531 and clearly indicated that the sample was a complex mixture of hydrocarbons of various structural types. The derimed liquid sample was therefore subjected to fractional distillation and each of the fractions and the residue were individually analysed by gas chromatography.

Individual fractions

During fractional distillation of the sample the dissolved C₂-C₄ hydrocarbons

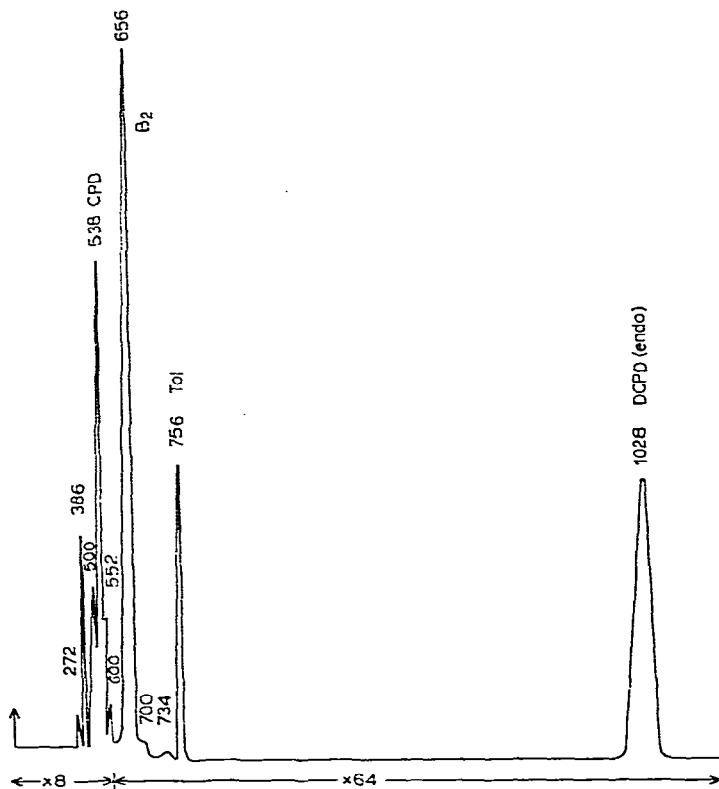


Fig. 3. Chromatogram of the composite sample on SE-30 at 100°. B₂, Benzene; Tol, toluene; other compounds as in Fig. 1.

were not recovered and the first drop was collected at 35°. However, the first fraction boiling in the range IBP–41° constituted less than 1% of the total and could not be analysed successfully owing to its high volatility. This fraction possibly consisted of C₂–C₅ hydrocarbons, as shown by the peaks with retention indices of 272–500 in the chromatogram of the composite sample in Fig. 3. These peaks were characterized as unsaturated compounds from the ΔI values.

The next cut (41–56°) was collected into two sub-fractions (41–55° and 55–56°). It is of interest that after the still-head temperature reached 55° it became remarkably steady and a large fraction boiling at 55–56° could be collected. This observation indicated that the 55–56° cut is apparently a pure component. However, none of the simple hydrocarbons was known to boil in that range and on subjecting fraction 2a and 2b (Table I) separately to chromatographic analysis it was found that qualitatively both fractions were similar in nature. Typical chromatograms of fraction 2b on SE-30 and TCEP are shown in Figs. 5 and 6. The major constituents in these fractions were identified as methanol, cyclopentadiene and benzene, with peak retention indices of 435, 549 and 658, respectively, on SE-30 (Fig. 5). The occurrence of benzene (b.p. 80°) in appreciable amounts in these lower boiling fractions was due to the formation of an azeotrope with methanol⁵.

It is of interest that although the constant-boiling mixture of benzene and methanol (fraction 2b) could be easily resolved on a non-polar SE-30 column (Fig. 5)

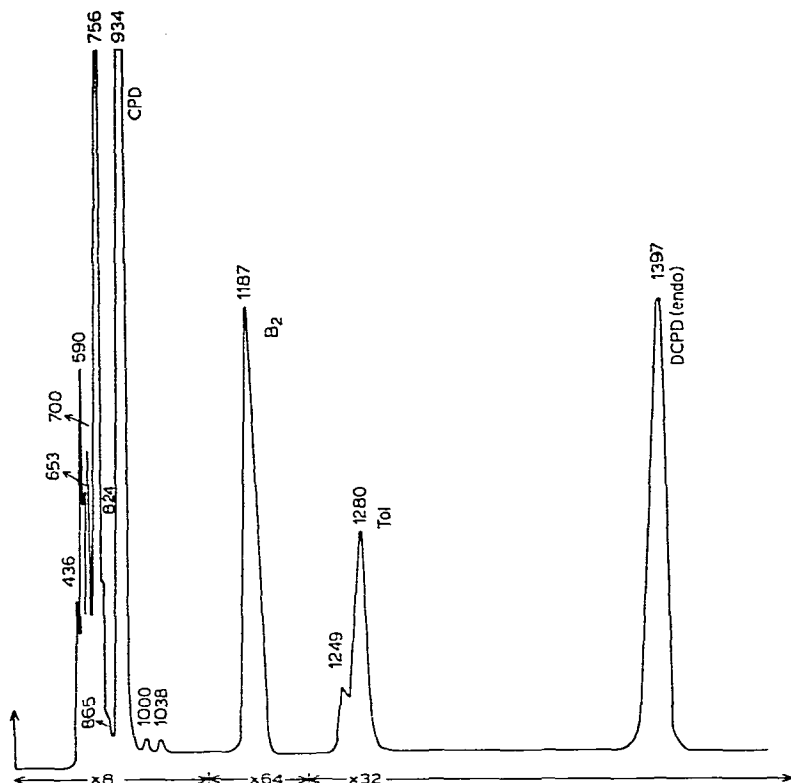


Fig. 4. Chromatogram of the composite sample on TCEP at 100°. Compounds as in Figs. 1 and 3.

into peaks with retention indices of 435 and 658 attributable to methanol and benzene, respectively, the separation could not be achieved on a polar TCEP column (Fig. 6), regardless of the column temperature used. It is apparent that on a TCEP column the peak with a retention index of 1215 represents a composite peak of methanol and benzene while the peak with a retention index of 968 could be assigned to cyclopentadiene. Peculiarly, the retention indices of pure methanol and pure benzene when injected separately on a TCEP column were 1190 and 1215 (difference 25) and 1170 and 1187 (difference 17) at 115° and 100°, respectively, the difference in retention indices being sufficient to effect a reasonable separation between the two. However, when injected together as a mixture, coincidence of peak retention indices occurred at 1215 (115°) and 1187 (100°) on the same TCEP column. At present the data offered are insufficient for a plausible explanation of this anomalous behaviour.

Chromatograms* run on fraction 3 at 100° showed five peaks and shoulders (*I* values from 500 to 656) on an SE-30 column and eight peaks and shoulders (*I* values from 700 to 1187) on a TCEP column. An increase in the number of peaks in going from a non-polar to a polar stationary phase was typical of mixtures containing isomeric unsaturated hydrocarbon systems of diverse polarity. The peak with a reten-

* The chromatogram run on fraction 3 is not reproduced as all of the constituents of fraction 3 were common to most of the components present in the composite sample. As such, the peak retention indices of fraction 3 can be easily seen from Figs. 3 and 4.

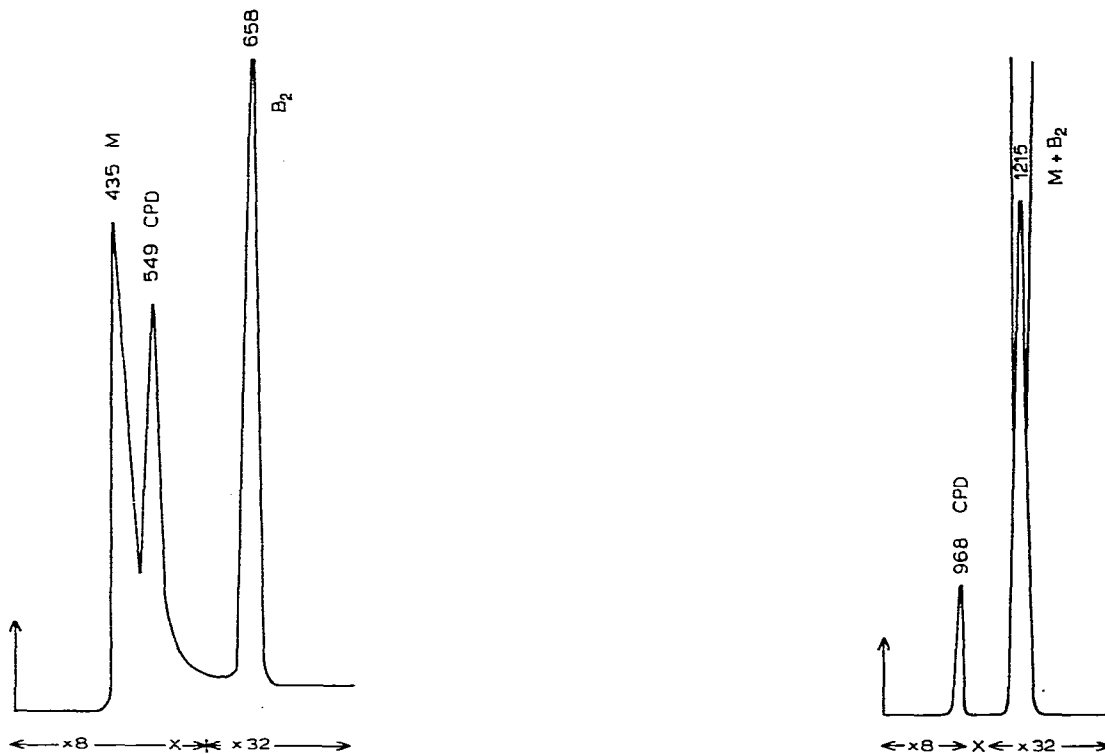


Fig. 5. Chromatogram of the 55–56° fraction on SE-30 at 115°. M, methanol; other compounds as in Figs. 1 and 3.

Fig. 6. Chromatogram of the 55–56° fraction on TCEP at 115°. Compounds as in Figs. 1, 3 and 5.

tion index of 538 obtained on an SE-30 column corresponded to a peak with a retention index of 934 on a TCEP column and could be attributed to cyclopentadiene. The major peak with a retention index of 656 on an SE-30 column corresponded to the major peak with a retention index of 1187 on TCEP column and was confirmed as benzene. The appearance of peaks with retention indices of 700, 756, 824, 865, 1000 and 1038 on a TCEP column corresponding to retention indices of 500, 552 and 600 on an SE-30 column indicated that most of the peaks in fraction 3 belong to compounds other than saturated hydrocarbons. The observed ΔI values, which ranged between 200 and 438, were indicative of the presence of unsaturated compounds such as diolefins and cyclo-olefins in this fraction. The I values of 500 and 600 obtained on SE-30 and their absence on TCEP indicated that *n*-pentane and *n*-hexane were not present in fraction 3. The appearance of cyclopentadiene (b.p. 41°) in the fraction boiling at 56–80° and its greater abundance in fraction 3 than fraction 2b was contrary to expectation. However, such an observation could be explained by considering the marked propensity of the dicyclopentadiene molecule to dissociate into its monomer at temperatures above 80°. Thus, during the course of distillation the free cyclopentadiene in the sample initially distils over and makes its appearance in the 41–56° fractions (fractions 2a and 2b). As the higher fractions are collected, however, the kettle temperature increases and causes the thermal dissociation of the dimer into cyclo-

tadiene, which in this way reappears in higher boiling fractions. A similar observation was made by Bhattacharya and Rao⁶ during the distillation of industrial coke oven benzoles containing cyclopentadiene.

Residue

The residue boiling above 80° gave four peaks on an SE-30 column and five peaks on a TCEP column. The chromatograms are reproduced in Figs. 7 and 8. Peaks with retention indices of 658 and 760 on the SE-30 column and the corresponding peaks with retention indices of 1215 and 1308 on the TCEP column were identified as benzene and toluene, respectively. The peak with a retention index of 1046, although appearing as a composite peak on the non-polar SE-30 column, could easily be resolved into peaks with retention indices of 1398 and 1445 on the polar TCEP column. By referring to the chromatogram of the standard sample (Figs. 1 and 2), these could be assigned to the *exo* and *endo* isomers, respectively, of dicyclopentadiene. Corroborative evidence was obtained from infrared spectroscopic studies. It may be noticed, however, that while in the chromatogram of the standard sample (Fig. 1) only slight tailing of the peak with a retention index of 1046 occurred, the tailing became greater in the chromatogram of the residue (Fig. 7). The cause of this tailing could be ascribed to the formation of increasing amounts of the *exo* isomer of dicyclopentadiene during distillation, which, owing to its near identical boiling point with that of the *endo* isomer, could not be separated on the non-polar SE-30 column. Thus, in the chromatogram of the composite sample (Figs. 3 and 4), no *exo*-dicyclopentadiene could be

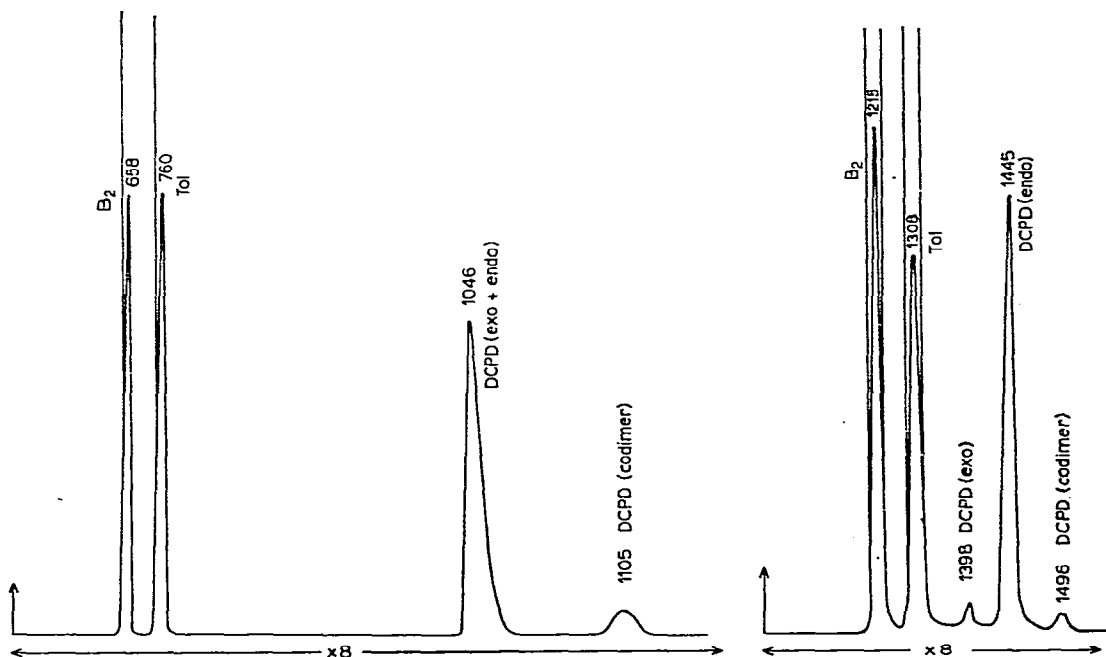


Fig. 7. Chromatogram of the residue boiling above 80° on SE-30 at 115°. Compounds as in Fig. 3.

Fig. 8. Chromatogram of the residue boiling above 80° on TCEP at 115°. Compounds as in Fig. 3.

detected on a TCEP column and consequently no tailing of this peak occurred on an SE-30 column, while in the standard sample, which contained about 89% of *endo* isomer and 1.8% of *exo* isomer, the tailing was only nominal. As, however, the residue was heated to about 100° in the distillation kettle the tailing became marked owing to the skeletal rearrangement of the *endo* configuration to the more stable *exo* form, as expected from the thermodynamics of the dimerization of cyclopentadiene⁷.

From a comparison of the chromatograms of the residue (Figs. 7 and 8) with those of original composite sample (Figs. 3 and 4) it is apparent that both of the peaks with retention indices of 1398 and 1496 on the TCEP column which appeared in the residue represent compounds that are reformed during distillation. Of these, the last peak, with retention indices of 1105 on SE-30 and 1496 on TCEP, could, on the basis of its ΔI value, at best be assigned to a cycloolefin with a structure resembling that of dicyclopentadiene, possibly a codimer of cyclopentadiene⁸.

CONCLUSION

The application of an extended concept of retention indices has been successfully demonstrated in identifying the components responsible for pipeline choking in the cryogenic separation of coke oven gas. The major factors in pipeline choking phenomenon, however, appear to be mainly the carry-over of reactive olefins, particularly cyclopentadiene, which undergoes polymerization/condensation to yield gummy substances. The formation of dicyclopentadiene at lower temperatures possibly occurs owing to the catalytic influence of oxides of nitrogen present in the coke oven gas. The other unidentified components present in the sample are characterized by their retention indices as unsaturated hydrocarbons such as olefins, diolefins and cycloolefins.

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