

# Stabilization of Nigeria Natural (Havea) Rubber with Bound Antioxidant Added as Masterbatch

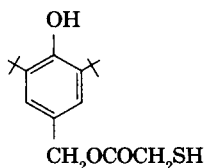
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## Synopsis

Nigeria natural rubber concentrates in a newly synthesized antioxidant were added as conventional additives for normal natural rubber. The natural weathering, thermal- and photooxidative protective performance of the adduct were examined by measurement of the carbonyl index and induction periods. From the results obtained, it is concluded that the addition of this new antioxidant in the form of masterbatch appears to be a better practical way of incorporating it into natural rubber simply by dilution of natural rubber. The bound stabilizers were found to be resistant to leaching.

## INTRODUCTION

In recent publications<sup>1-3</sup> it has been reported that antioxidants and UV stabilizers containing the thio group can be chemically reacted with latex to give the masterbatch of polymer bound antidegradants. The synthesis of such masterbatches is clearly of some commercial importance and appears to be a good and convenient way of incorporating additives in polymeric systems. Thus one feels that the development of a general method of binding antioxidants to rubber by antioxidant-thio addition to natural rubber latex before vulcanization should provide a unique opportunity to test the importance of masterbatching technique. In the present study, 3,5-ditertiary butyl-4-hydroxybenzyl thioglycollate (DBHBT) (I) containing a typical antioxidant structure was reacted with Nigerian natural rubber latex to give the corresponding adduct, and its protective performance was examined. This is a continuation of a series of test we are carrying out to show that this new antioxidant is a good thermal stabilizer for both saturated<sup>4</sup> and unsaturated systems.<sup>1,2</sup> It should be noted that natural rubber is hardly used in its natural form but always in the presence of other ingredients; the present emphasis is, however, on the performance of DBHBT as a thermal stabilizer for rubber:



(I) DBHBT

## EXPERIMENTAL

### Materials

The normal hevea rubber (34% solid content) used in this work was collected in the month of July from clones Harber I and Tjiri, field MN4 of the Rubber Research Institute of Nigeria, Bendel State of Nigeria. It was preserved by adding ammonia to the fresh latex. Cumene hydroperoxide and hydrated 4,4-azobis (4-cyanovaleric acid) were supplied by Polysciences Inc. and Aldrich, respectively. All other reagents of analytical grades were supplied by British Drug Houses Ltd., 3,5-ditertiary butyl-4-hydroxybenzyl thio glycollate (DBHBT) was synthesized as previously described.<sup>2</sup>

### Preparation of DBHBT modified Natural Rubber Latex

An aqueous emulsion of DBHBT was prepared as follows: 0.5 g stearic acid was melted with 8.0 g DBHBT at 75°C. The molten mixture was slowly added to 25 cm<sup>3</sup> of 0.7M NaOH, and the mixture thoroughly stirred and quickly cooled. The emulsion was usually melted and purged with pure nitrogen before addition to the mixture.

Some 293 cm<sup>3</sup> of 34% (100 g dry rubber) natural rubber latex was diluted with distilled water and stripped. The stripped latex was then partially deammoniated by passing pure nitrogen at room temperature until the pH fell to between 8.0 and 8.5. In a preliminary set of experiments the optimum temperature, time, and pH required to maximize the effectiveness of chemical binding of the compound were examined. In the grafting reaction a redox system was used. In this procedure the emulsion of the DBHBT was added and maintained in aqueous suspension under turbulence and brought into contact with the latex. The reaction was carried out at 67°C. Cumene hydroperoxide (pure) initiator was added in aliquots within 2 h. The reaction was continued for a further 7 h. The pH was maintained as closely as possible between 8.0 and 8.5 in order to prevent coagulation.

At the end of the reaction, the latex was coagulated by addition of dilute formic acid and the coagulum washed several times to remove free acid. The coagulum was dried *in vacuo* at room temp (25–30°C). The experiment was repeated using hydrated 4,4-azobis (4-cyano-valeric acid) as initiator. It was found that the extent of binding in the grafting reaction using cumene hydroperoxide was about 20% while the extent of binding in the grafting reaction involving the cyanovaleric acid was 7%.

### Determination of Extent of Binding

The extent of binding of DBHBT was determined by the following procedure: 10.0 g of dry rubber adduct was exhaustively extracted for 48 h in a soxhlet extractor using a hot mixture of 1,1,1-trichloroethane, acetone, and methanol under nitrogen atmosphere. After extraction the rubber adduct was dried under vacuum. Extraction time had been previously determined in preliminary experiment as follows: The amount of DBHBT left in the batch was monitored by IR and UV until no more was removed. It was found that 48 h was sufficient to remove all the uncombined antioxi-

dant. An aliquot consisting of a suitable volume was evaporated to dryness in a rotary evaporator; then quantitative determination of the extracted antioxidant was carried out by the technique previously determined.<sup>1</sup>

### Film Preparation

All dilutions were made from the 20% masterbatch. Films were cast from 2% benzene solutions of the extracted adduct diluted to desired concentrations with unmodified natural rubber. The solvent was evaporated at room temperature from measured volumes of solutions placed on the surface of clean mercury in a desiccator. An atmosphere of nitrogen under reduced pressure was maintained for 48 h. The films were finally dried *in vacuo* at room temperature. The unmodified natural rubber was similarly treated. Films of 0.15 mm thickness were used in all the experiments.

### Degradation Procedures

**Photooxidation Experiments.** Ultraviolet irradiation experiments were conducted on the films at a temperature of about 35°C in air with UV lamps emitting 365 nm lines. The degradation of the films was followed by running the IR spectra at regular intervals.

**Oven Aging Experiments.** Accelerated thermal aging experiments were conducted on the films in a Wallace oven at 80°C and with an air flow rate of 3 ft<sup>3</sup>/s. Each sample film was contained in a separate cavity. Degradation was then followed by running the IR spectra of the films before heating and at regular intervals during heating.

**Natural Weathering Experiments.** The outdoor weathering of the films was carried out by exposing the films in the open air at the geographical experimental station of Ahmadu Bello University, Zaria, on latitude 11° N

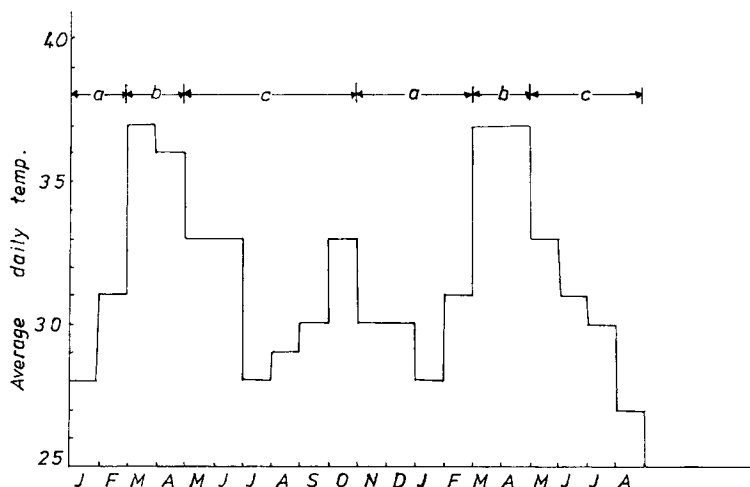


Fig. 1. Average daily temperature (maximum) and general weather conditions in Zaria for the years 1981-1982. (a) Oct.-Feb., Harmattan period. Dry and cold, minimum daily temperature as low as 10°C; daily relative humidity 21%; (b) heat period—very hot and humid, average daily temperature (max) up to 37°C. Average daily relative humidity 50%; (c) rainy season—cool and humid, daily temp (max) about 30°C, relative humidity 75%.

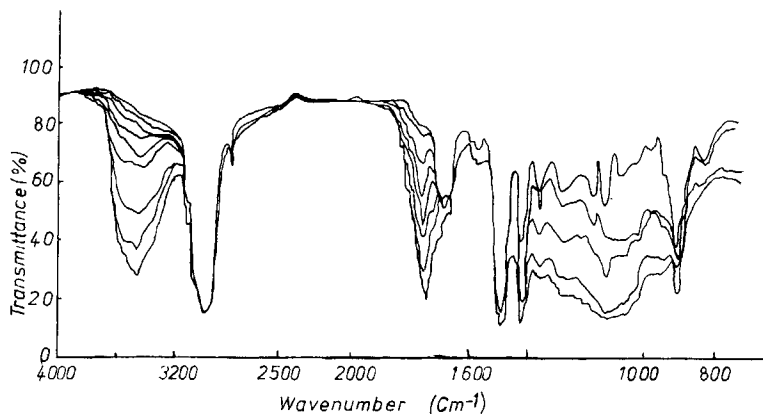


Fig. 2. Infrared spectra of Nigeria natural rubber during photooxidation.

and longitude 7.5° E. Sample films were mounted between two very thin plywoods in which holes of appropriate dimensions were cut out. The film samples were centrally placed over the holes on one sheet before placing the other on top. The system was clamped to hold the films in position, and weathering was allowed to proceed. Films of even thickness of 0.15 mm were used for the measurements.

The work being reported here was carried out between July 1980 and August 1982. During this period the rubber samples experienced the aggressively varying weather conditions of this country. During this period the daily temperature varied between 27°C and 37°C (Fig. 1). The atmospheric conditions varied through dry and cold weather during the harmattan to hot and humid and to hot and wet.

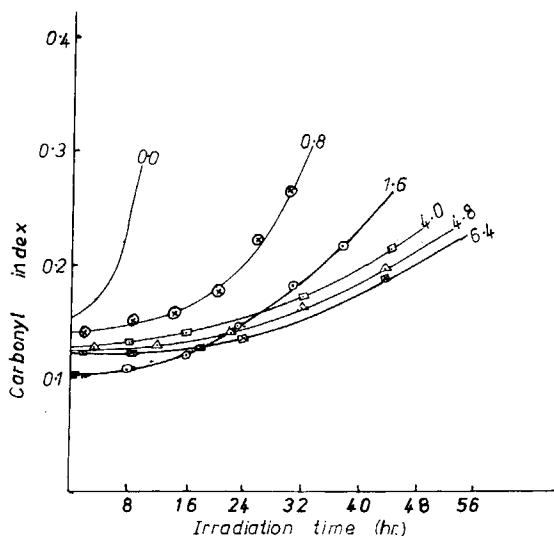


Fig. 3. Photooxidation of natural rubber. Dependence of carbonyl index on UV irradiation time for natural rubber containing varying concentrations of DBHBT added as masterbatch (after extraction). Numbers on the curves are masterbatch concentrations (%).

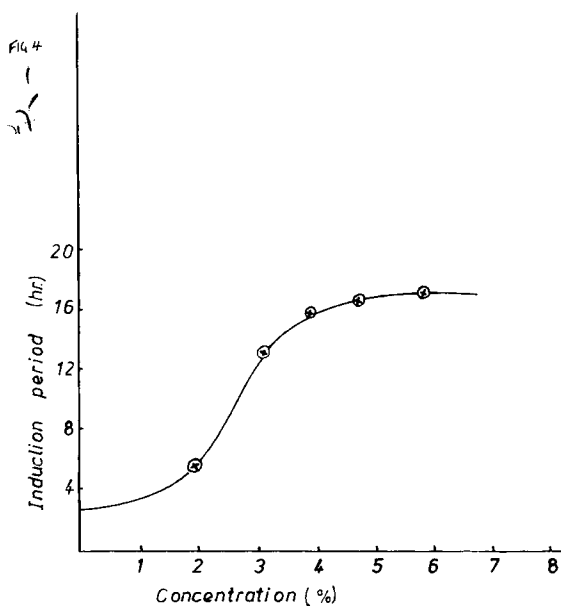


Fig. 4. Effect of masterbatch concentrations on the photostability of natural rubber.

**Instrumentation.** Since over 50% of the oxygen absorbed by elastomers go to form carboxyl, carbonyl, and/or ester groups,<sup>5</sup> IR absorption spectra have been found useful in following the changes in the microstructure resulting from oxidation. In all the aging experiments, the structural changes taking place in the films were monitored by IR spectra in the region  $600\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . These changes were recorded by a conventional

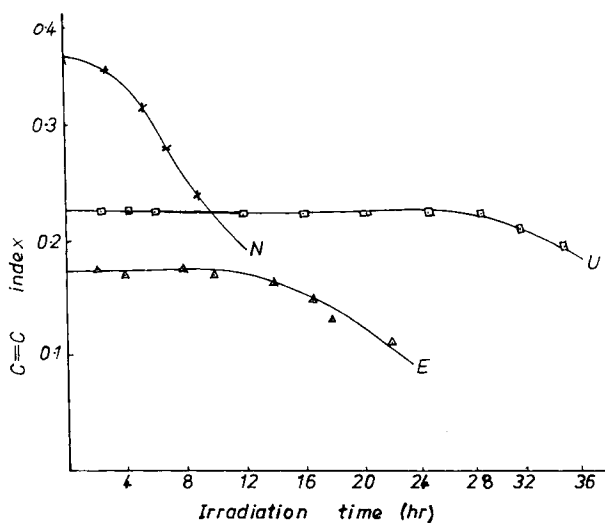


Fig. 5. Photooxidation of natural rubber. Effect of UV irradiation on the C=C bond indices; U = unextracted, E = extracted, N = natural rubber.

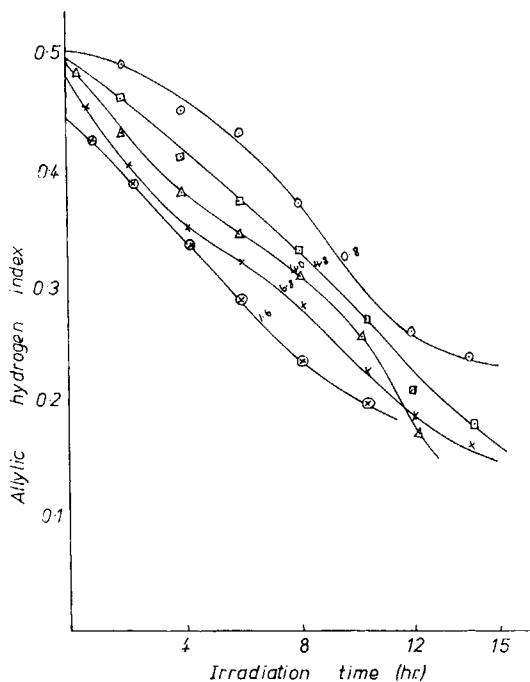


Fig. 6. Effect of UV irradiation on allylic hydrogen atoms. Numbers on curves are masterbatch concentrations (%).

double beam spectrophotometer, Perkin-Elmer Model 700 IR. For the evaluation of degradation due to natural weathering, UV or thermal oxidation, the peak intensities of the relevant bands were measured by the use of base line method. The ratio of these peaks intensities to that of an invariant peak at  $2910\text{ cm}^{-1}$  (indices) were plotted as a function of oxidation time.

## RESULTS AND DISCUSSION

The stability of modified natural rubber toward natural and accelerated environmental weathering has been studied.

Figure 2 shows typical spectra changes occurring during photooxidation of modified extracted natural rubber. In all the studies the modified natural rubber in the form of masterbatches has been used as an additive for natural rubber. There are marked band formations at  $1720\text{ cm}^{-1}$  assigned to saturated carbonyl groups and  $3500\text{ cm}^{-1}$  assigned to the hydroxyl and hydroperoxide groups. These peaks are seen to grow progressively with irradiation time. Band decay is also noticed in the bands at  $1380$  and  $860\text{ cm}^{-1}$  assigned to methylenic and allylic hydrogen atoms, respectively.<sup>6</sup> Pronounced spectra changes are found in the region between  $900$  and  $1400\text{ cm}^{-1}$ . In this present report, we have used changes in the well established carbonyl index method to follow degradation.

Figures 3-6 show the plots of the changes in the various indices of the films at varying concentrations of added masterbatches. It was found that the unstabilized natural rubber softened and ruptured within 2 h of exposure to UV light. This proves the great instability of NR to UV light.

Figure 3 represents the plot of carbonyl index as a function of irradiation time. All together, six concentrations of masterbatches to give different amounts of bound antioxidant were added to NR. The figure clearly reveals the chemical changes taking place during photooxidation of NR. All the films exhibit some induction periods showing that the bound DBHBT diluted to various concentrations has some protective power against photodegradation.

Figure 4 shows the dependence of the induction periods upon concentration of masterbatch. The figure shows that the degree of stability is dependent upon concentration. Maximum activity seems to have been reached at about 4.8%, and thereafter there is no further increase in induction period with increase in concentration of bound stabilizer. That is to say, the most economical concentration giving maximum efficiency should be 4.8% adduct per 100 g natural rubber.

Figure 5 shows the plot of loss in unsaturation against irradiation time for extracted and unextracted modified samples. Compared with the unmodified natural rubber, the modified rubber remains highly protected even after extraction. In other words, grafting of the antioxidant onto rubber makes the rubber resistive toward environmental degradation because the antioxidant cannot be extracted or leached. All the blends made from the masterbatch exhibit induction periods. The double bonds appear stable to photooxidation. Also methylenic hydrogens also appear to be stable to photochemical attack. The allylic hydrogens are seen to be quite susceptible to uv attack as seen in Figure 6. Unlike the other functional groups, the allylic hydrogen groups display no induction periods. This therefore suggests that the primary reaction which lead to photodegradation of modified natural rubber begins with the abstraction of allylic hydrogen atoms and not an initial attack on the double bonds, which is the case with some synthetic rubbers.<sup>1</sup>

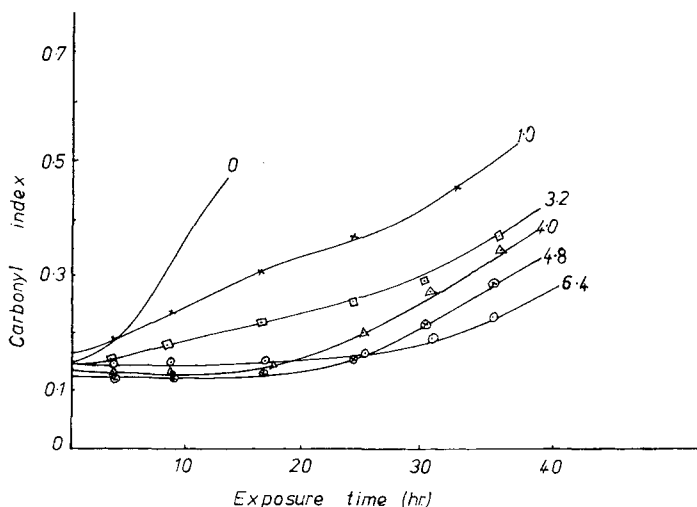


Fig. 7. Natural weathering of Nigeria natural rubber. Dependence of carbonyl index upon outdoor exposure time at varying concentrations of added masterbatch. Numbers on curves are masterbatch concentrations.

## NATURAL WEATHERING

In selecting appropriate stabilizers for polymeric materials used in the manufacture of commercial articles, it is very essential to evaluate the efficiencies of the additives in the environment where such articles will be used. The efficiency is influenced by various factors, one of the most relevant being the loss of stabilizer by diffusion and evaporation. Most of the workers on stabilization of polymers focussed attention mainly on volatility of stabilizers during fabrication. Because of the nature of our natural environment loss of stabilizers due to evaporation, diffusing and leaching have proved to be a major source by which additives are lost from polymeric products.<sup>7</sup> In this study the modified natural rubber films were exposed outside at various times of the year so that the films experienced the aggressively varying weather conditions.

Figure 7 represents a typical graph of carbonyl index against exposure time. The experiments were repeated several times over the years. The figure reveals that the presence of bound DBHBT in rubber protects the natural rubber from instantaneous degradation. Under these circumstances, the optimum activity is obtained at a concentration of 6.4 g stabilizer per 100 g natural rubber. As can be seen from the graph, the higher concentrations of additives exert little protection. The maximum induction period obtained is about 25 h. The mechanism of oxidation or stabilization of natural rubber is complex under natural environment. The numerous environmental factors may exert different amounts of influence at various stages of degradation and at different concentrations of DBHBT. Nevertheless, DBHBT bound to natural rubber seems to impart some stability to natural rubber. The unmodified film could not withstand the natural conditions for a period of more than 3 h during the months of March–June but could go up to 5 h July–September.

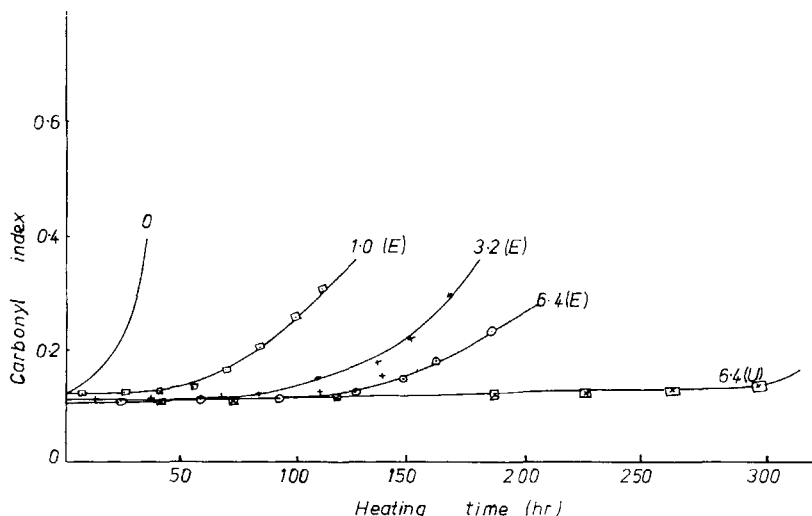


Fig. 8. Thermal degradation of natural rubber containing different amounts of DBHBT added as rubber adduct masterbatch. Number on curves are concentrations of masterbatch (%). The rubber was oxidized in air at 80°C.



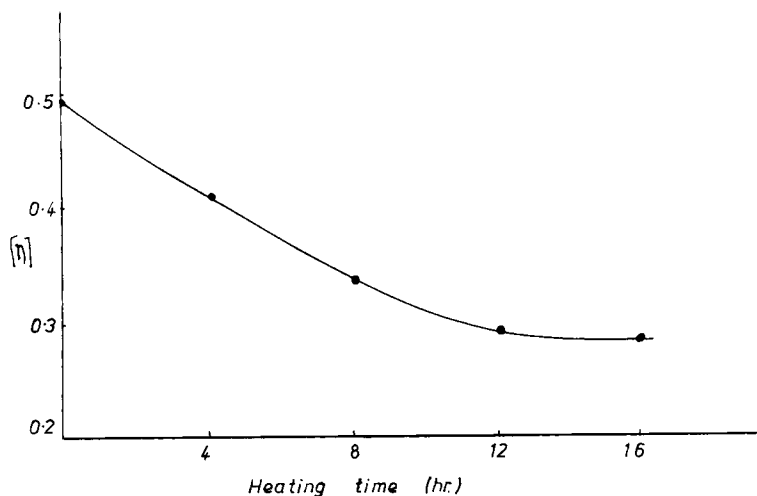


Fig. 9. Thermal degradation of natural rubber. Dependence of limiting viscosity ( $\eta$ ) on the heating time.

### Air-Oven Aging

Figure 8 shows the plot of carbonyl index as a function of heating time of the masterbatch adduct diluted to various concentrations for the extracted (E) and unextracted (U) samples. It is clear from Figure 8 that the bound DBHBT is an excellent thermal stabilizer for natural rubber. All the various concentrations used give very long induction periods. The unextracted samples exhibit longer induction periods than the extracted samples. With this finding it is being concluded that DBHBT will be a good thermal stabilizer for Nigeria natural rubber.

Figure 9 shows the plot of limiting viscosity against time for the rubber heated in an air oven. The graph shows that the limiting viscosity decreases with increase in heating time. No gel was formed. This means that the mode of thermal degradation is by chain scission.

### CONCLUSION

It is concluded that DBHBT could be grafted onto natural rubber in the latex stage. The bound antioxidant, though primarily not a UV stabilizer, offered some stability against photodegradation. It also protected the rubber against environmental degradation. The bound antioxidant offers excellent thermal stabilization when the films were heated in an air oven. The induction periods in all the degradation modes were found to be concentration-dependent, reaching an optimum activity at 4.8 g stabilizer, 100 g natural rubber during photooxidation. Thermally all concentrations offer considerable protection. Thus from the foregoing it could be said that the addition of DBHBT in the form of masterbatch appears to be a practical way of incorporating it in natural rubber simply by dilution of natural rubber and

gives good thermal and stabilizing effects that cannot be achieved by the additive if added in the conventional way.

It must, however, be mentioned that natural rubber is hardly processed alone; other ingredients have to be added, and they will greatly affect these properties.

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