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A Study on Composite Panels Prepared from Mixture of Mineral Adducts with Calabrian Pine Tree (Pinus brutia) Residues

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Abstract – The heat transfer coefficient values of 0.250 W/mK and λ: 0.261 W/mK were found for Type 1 boards (bark based experimental boards of XB_I and YB_V) and λ: 0.321 W/mK and λ: 0.311 W/mK were found for Type 2 boards (cone based experimental boards of XC_V and YC_{II}), respectively. But all these are lower than standard value of 0.065 W/mK. However, visual evaluation show that all samples have low flame spreading properties which did not reach the threshold limit of 150 mm under a single flame combustion test. All Type 1 boards show lower mass loss (w, %) than control sample (B_0: 11.97%), regardless of mineral additive type and proportions. The lowest mass loss of 6.36% was obtained with sample of YB_{IV}. It is noticeable that olivine-cone (YC) and olivine-bark (YB) based panels usually show lower mass loss than dolomite-cone and dolomite-bark based panels at similar experimental conditions. The surface burning tests clearly indicate that the both mineral additions have lowering effects on burning feature of boards. This is probably olivine and dolomite could be absorbing heat and release water. Hence the burning area might become colder during evaporation of water with increasing charring and improve insulation of materials. The heat insulation levels of boards have found to be closely related with mineral content. But olivine seems to more effective for improving insulation properties for Type 1 boards. It is also found that both type panels (Type 1 and 2) which prepared from various proportions of dolomite and olivine as additives (10-50%) were show higher resistance against thermal degradation than control panels which prepared only (100%) from lignocellulosic material (cone and bark).

Keywords – Dolomite, olivine, red pine cone, red pine bark, fire resistance, heat properties, TGA.

I. INTRODUCTION

The wood-based composites have been on the market for over decades. Since they have become fabricated, the usage of those materials has been considerably increasing every year. These materials are engineeringly design products which created by combining several different materials in network in order to gather the most superior properties in one material [1-2]. However, these products take advantage of wood in its high fracture toughness, strength to weight ratio, low cost, flexibility during processing, thermal and acoustic resistance, while the synthetic thermo-set adhesives act as binder [1-3]. Beside many advantages of these products, they are also much better suited to fire, bio-deterioration and weathering applications to which solid woods are vulnerable [3]. Most of the research in the field of bio-composites deals with chipboards, fiberboard and plywood that compatibility of wood and non-wood species with synthetic adhesive [3]. More recently, oriented strand board and wood beams have been manufactured [4]. In the field of composite manufacturing and reinforcement, optimization of additive contents plays a significant role in enhancing the engineering properties of materials; but it is a challenge to develop analytical solutions for optimal combinations [4-7].

The researchers and industries are exiting on developing sustainable/greener technology to minimize the impact on the circumventing environment [8-9]. There is a desideratum to found incipient supplementary lignocellulosic material and additives that would show kindred or superior interaction in composite [10-12]. However, besides wood, agricultural wastes, forest residues and many annual plants that have limited economic values, have been suggested to be useful in lignocellulosic panel manufacturing. Recent studies investigated suitability of some orchard wood's pruning wastes which have similar chemical and physical properties to woods (softwoods and hardwoods used in wood products industry) which could be useful in experimental particleboard manufacturing [13]. It has been suggested that pine cones can be an alternative raw material source for the forest products industry due to their morphological, chemical and physical properties [14]. It has explained that experimental particleboards prepared with mixture of red pine- wood chips, cone and barks have some level high weathering performance under external atmospheric conditions [15].

In these days, the massive growth and extension of the construction industry, there is a prerequisite for an immense amount of material such as lignocellulosic and adhesives in forest products industry [16]. Thus, manufacturing of alternative composite production might emit greenhouse gas and consumes energy in an immense amount of energy [17]. To overcome these issues, the best solution is to utilize alternative sources (wastes, residues) by using them as supplementary composite materials, which avails in the conservation of nature's deposits, reduces the landfills spaces, abates the paramount quantity of energy needed for the manufacturing [16-18].

Dolomite is a sedimentary rock primarily utilized in building and road construction work [11]. It has already proposed that dolomite could be used for producing as substitute in sand bricks, in asphalt concrete, and metallurgical purposes [11, 19]. Similarly, due to the abrasive feature of olivine mineral, it has been started to use for cleaning buildings, roads and provide heat and sound insulation as rock wool [11,20].

Currently, there is very limited information about the effects of olivine and dolomite as additive to lignocellulosic matrix. In recent study, it has speculated that addition of dolomite mineral into wood-based fiberboard matrix negatively affects the physical and mechanical properties of the boards such as water absorption, thickness swelling, bending resistance and elasticity modulus in board structure, but the fire resistance properties of boards increase [21,22]. However, in various research works, some information based on dolomite and olivine usage has been investigated recently to provide a view of their properties. But a research is needed to get the information on their performances in the bio-based composite manufacturing. Therefore, this study presents a study of dolomite and olivine as a substitute granular material in composite matrix and its effect on various properties.

II. Material And Methods

Calabrian pine tree (*Pinus brutia* Ten.) residues of bark and cones were obtained from Isparta region in Turkey. The red pine cone and barks were turned to chips at laboratory type hammer mill. The chips were screened to 1-3 cm particles and dried in the oven at 105 (± 3 °C) until they reached 2-3% moisture content. The bonding agent employed was urea-formaldehyde resin supplied by a commercial operated particleboard plant, in Turkey. It has 65% solid content and 20% ammonium chloride hardener, utulized as received. The glue was applied 10% and hardener was 1% in the test boards by weight based on oven dry material. The target densities of the manufactured boards were 0.9 gr/cm^{-3} (± 0.1 g/cm^{-3}); a total of 72 boards (three from each conditions) were made with the dimensions of 420x330x10 mm. The detailed information on board preparation can be found elsewhere [11].

The standard test method for Thermal Conductivity of Refractories by Hot Wire (Platinum Resistance Thermometer Technique) was used to determine thermal insulation behavior of composites according to ASTM C 1113-90 Hot Wire Method. For determining mass burning rate, the test samples were cut as standard dimensions of 100x100x10 mm pieces and placed on the test apparatus at vertical position. The boards were flamed at approx. 800 °C with the distance of 30-50 mm from the heater surface in duration of 5.0 min. At the end of test, the boards were weighted and mass loss calculated based on weight differences. TGA/DTA analysis of the sample was performed with a thermogravimetric analyzer (Seiko SII TG/DTA 7200, TA Instruments). Analyzes were performed under a nitrogen flow of 60.0 ml/min and the samples were heated from room temperature to 80°C in 10.00C/min. The weight of each sample at baseline (original condition) was measured at approximately 5 mg in TGA analysis. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier spectrometer.

The flammability of the sample was examined with the flammability test according to the TS EN ISO 11925-2 standard and mass loss is calculated. In the combustion behavior experiment, the temperature differences on the surface were determined by placing the sample between the flame source and the infrared measuring device.

While many combinations were tested, some code number and abbreviations were established throughout the study given in Figures and Tables. These are; **X:** Dolomite, **Y:** Olivine, **B:** Bark chip in mixture (bark type boards), C**:** Cone chip in mixture (cone type boards), **X-/YI, II, III, IV and V:** Dolomite and olivine proportions in mixture (w, gr, %) of 10-,20-,30-,40- and 50%, respectively.

III. Results And Discussions

The thermal conductivity values of the samples obtained with the addition of dolomite and olivine are given in Table 1. For the dolomite-bark based panels (XB types), the lowest heat transfer coefficients were measured as λ: 0.250 W/mK) in XB_I, for the dolomite-cone based panels (XC types), it was found to be λ: 0.321 W/mK in XC_V. For olivine-bark based panels (YB types) it was found to be λ: 0.261 W/mK in YB_V for olivine cone-based panels (YC types), it was found to be λ: 0.311 W/mK in YC_{II} panels.

Table 1. Heat conduction coefficients (λ; W/mK) properties of experimental panels

Boards	**X**	**Y**
Mineral-red pine bark-based panels		
B_0	0.391	0.391
XB_I-YB_I	0.250	0.283
XB_{II}-YB_{II}	0.303	0.301
XB_{III}-YB_{III}	0.285	0.272
XB_{IV}-YB_{IV}	0.384	0.263
XB_V-YB_V	0.284	0.261
Mineral-red pine cone-based panels		
C_0	0.441	0.441
XC_I-YC_I	0.436	0.339
XC_{II}-YC_{II}	0.342	0.331
XC_{III}-YC_{III}	0.331	0.326
XC_{IV}-YC_{IV}	0.332	0.498
XC_V-YC_V	0.321	0.430
Standard	If <0.065, *thermal insulation material*	

Figure 1 shows visual evaluation of the boards that a single flame combustion tests were carried out to determine behaviors against flame according to TS EN-ISO 11925-2 standard (Fig. 1A) and burning feature of samples (Fig. 1B). According to visual observation, it was found that the flammability limit on the surface of any sample did not reach the threshold limit of 150 mm. Hence, all boards (bark and cone types) look like pass that test and shown little spread to char on surface and hence recorded as negative against ignition or flame spreads.

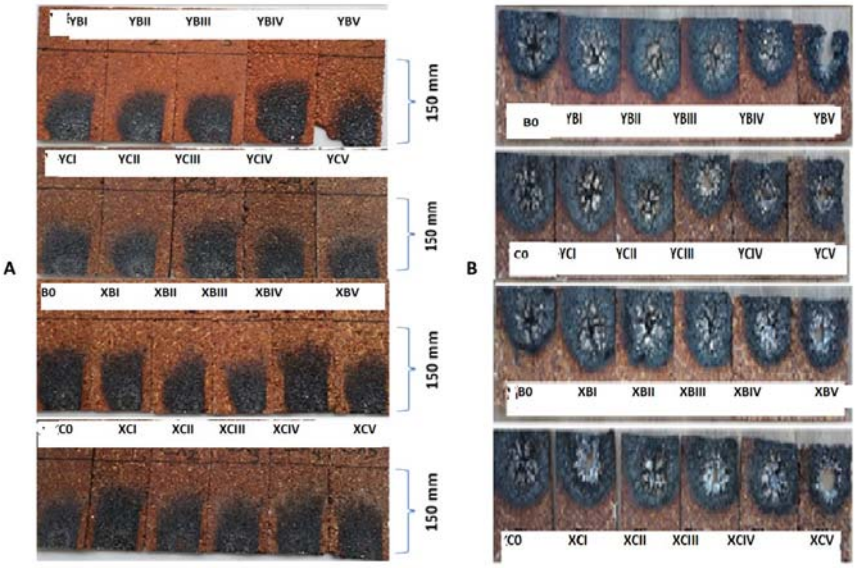

Figure 1. Visual evaluation of single source flame spreading (A) and burning features (B) of samples

However, after evaluating insulation and burning feature of samples, a single flame combustion test was conducted with 60-second intervals in total of 300 seconds durations and the measured weight loss (%) are comparatively plotted in Figure 2. For bark type boards, all samples show lower mass loss (w, %) than control sample (B_0: 11.97%), regardless of mineral additive type and proportions. The lowest mass loss of 6.36% was obtained with sample of YB_{IV}. For cone-based boards, only sample of XC_I show higher mass loss (21.55%) than control (C0: 15.76%) while rest of cone-based samples show lower mass losses than control. The lowest mass loss value of 10.16% was obtained with sample of YC_V, followed by 12.27% (YC_I) and 12.88% (YC_{III}). Weight loss is a factor that directly represents the flammability of materials, so the higher the weight loss represents the higher its flammability. It is also noticeable that olivine-cone and olivine-bark based panels usually show lower mass loss than dolomite-cone and dolomite-bark based panels at similar experimental conditions. However, the results clearly indicate that the both mineral additions have positive impact on burning behavior properties some level, in other words the flammability feature of boards decreased. This is expected considering olivine and dolomite have very high melting points and high resistance against fire. It has already proposed that, olivine and dolomite could be absorbing heat and release water. Hence the burning area might become colder during evaporation of water with increasing charring and improve insulation of materials [11].

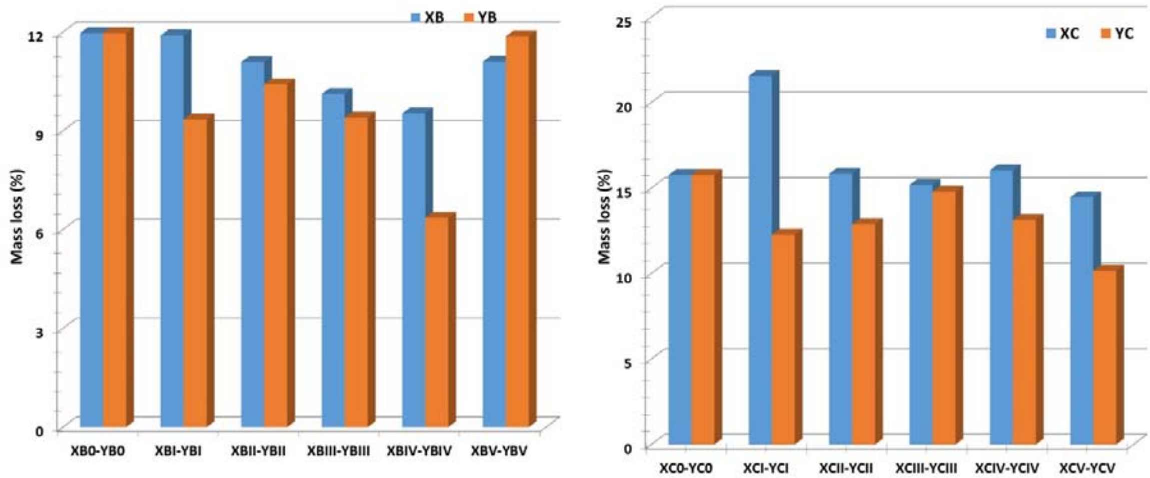

Figure 2. The mass loss of the samples after combustion

Figure 3 show the insulation properties of experimental panels, comparatively. It is observed that the insulation levels of boards have closely related with mineral content. But Figure 4A and B clearly implying that olivine is more effective for improving insulation properties for bark type boards. Except sample of BX_V, rest of experimental panels that prepared from dolomite-bark at various proportion show lower heat insulation properties than bark type panels that prepared from olivine-bark (BY type panels). The lowest measured surface temperature of 80.5 ^{0}C was found with sample of BY_{IV}, followed by 90.3 ^{0}C with sample of BY_I and 99.4 ^{0}C with sample of BY_{II}. (BO: 118.6 ^{0}C). For cone type panels, only sample of CY_I show lowest surface temperature value of 120.5 ^{0}C while rest of boards show higher surface temperature than control sample (C_0: 143.5 ^{0}C). It appears to both minerals are not effective for lowering heat transmission or improving thermal insulation properties of cone type boards.

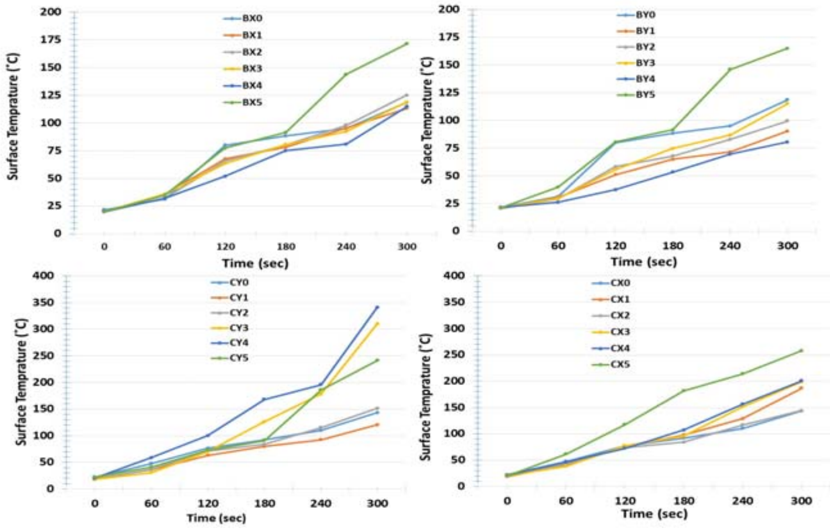

Figure 3. The insulation properties of experimental boards

The thermal degradation behaviors of experimental panels are comparatively given in Figure 4. It can be seen that both type panels (bark and cone) which prepared from various proportions of dolomite and olivine as additives (10-50%) are show higher resistance against thermal degradation than control panels which prepared only (100%) from lignocellulosic material (cone and bark). When Figure 4 are examined carefully, more less similar plot shape observed but controls show higher level degradation (mass loss) than mineral added samples. It was occurred 5-8% mass loss as a result of drying which caused by the humidity in the samples up to 100 ˚C. The sample mass loss remained approximately constant between 110-200 ˚C and no water remained in the cell wall. After 250 ^{0}C, heating started in organic materials. It has been determined that there are basically two deteriorations in the samples. The first of these was formed with a rapid slope in the range of 250-400 ^{0}C and mass loss was about 40-50%. At this level, molecular change has taken place. The other deterioration occurred in the range of 400-750 ^{0}C, with a less slope compared to other temperature distortions, and the mass loss in the samples reached 70-80%.

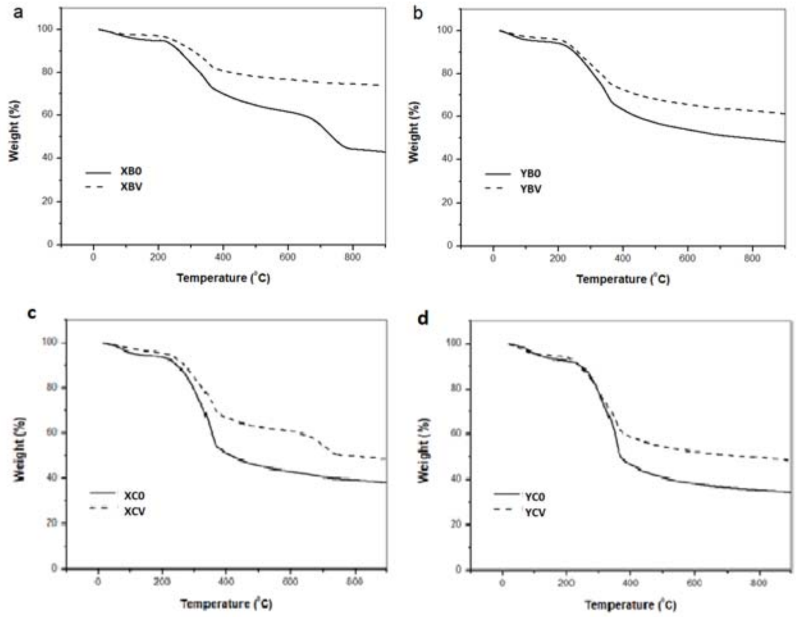

Figure 4. Thermal degradation (TGA) behavior of boards

TGA analysis at four different temperature degradation and mass loss properties are given in Table 2. It was divided three different temperature level as; starting temperature (Tb), first maximum temperature (Tm) and final temperature (Ts). The cone control panels show 16 ^{0}C (at tm) to 26 ^{0}C (at Ts) higher degradation temperature level than bark control sample. However, the highest initial degradation temperature was found with sample YC_V (Tb: 215 ^{0}C), the highest first maximum temperature was found with sample XC_V (Tm: 357 ^{0}C) and the highest final degradation temperature was found with sample YB_V (Ts: 537 ^{0}C). When the Table 2 carefully overviewed, for cone type boards, the lowest mass loss at all temperature levels was in the sample of XC_V which produced from pine cone-dolomite mixture at 1:1 (w/w) in proportion (Tb: 5.89-, Tm: 36.32-, and Ts: 45.51%). For bark type boards, the lowest weight loss at initially (Tb) was found with sample YB_V (5.06%), and XBV sample show lower mass loss at Tm (25.31%) and at Ts (39.75%).

Table 2. Thermal degradation (TGA) and mass loss properties of boards

Board Code	Tb (^{o}C)	Mass Loss (%)	Tm (^{o}C)	Mass Loss (%)	Ts (^{o}C)	Mass Loss (%)
Bark type boards						
B_0	189	5.63	352	31.06	420	40.09
XB_V	206	5.56	344	25.31	531	39.75
YB_V	177	5.06	344	30.13	533	44.4
Cone type boards						
C_0	205	7.4	350	41.52	446	57.39
XC_V	197	5.89	357	36.32	433	45.51
YC_V	215	8.03	351	41.53	400	53.4

The comparative Fourier Transformation Infrared Spectroscopy (FTIR) spectra presented in Figure 5. In general, peaks in the range of 700-1100 cm^{-1} and 1145-1162 cm^{-1} are assigned to C-O and C-O-C tension in polysaccharides (cellulose & hemicellulose). However, 1500-1610 cm^{-1} are C=O and COO-symmetric tension vibrations in aromatic rings that considered to a characteristic peak for lignin components [23,24]. In our study, the frequency of bands showing the characteristic structure of cellulose, lignin and hemicellulose in the FTIR spectrum of red pine bark (Fig. 6A) and cone (Fig. 6B) boards can be explained by the abundance of functional groups in the chemical structure [25]**.** There is not much differences were found between spectrum of XB0 and XBV; XC_0 and XC_V. But the he spectra of YBV and XCV show some wide bands at the 800-1550 cm^{-1} and 2900-3500 cm^{-1} which indicates some further OH- and groups in structure of material.

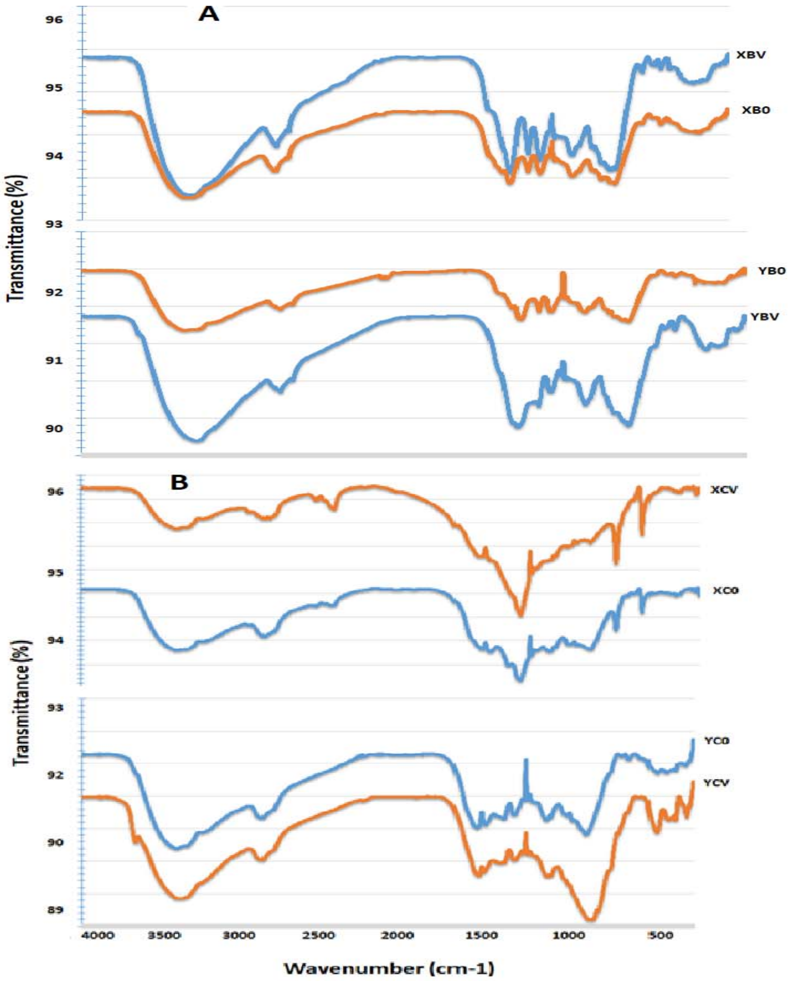

Figure 5. FTIR spectra of experimental boards (A: Bark type boards, B: cone type boards)

IV. Conclusions

The adducts of mineral substances of dolomite and olivine minerals with pine cone and bark chips as forest residue in the board structure was investigated. However these hybrid composites show some comparable technological properties when used certain proportions. It was demonstrated that calabrian pine tree residues of cone and bark as waste materials could use in the production of boards with mineral mixture in some proportions. Although addition of the mineral substances to mixture lowering effects on some properties but in some cases dolomite and olivine minerals contribute positive effects such as heat insulation and burning properties. It could be suggested that these panels could be useful in some places where heat resistance is neccessity. It is important that the experimental board formulations is very important which the application of dolomite and olivine should improve efficiently.

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