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Oxidative Desulfurization of Fuels Catalyzed by V₂O₅ in Ionic Liquids at Room Temperature

Dan Xu, Wenshuai Zhu, Huaming Li,* Jingtong Zhang, Fang Zou, Hua Shi, and Yongsheng Yan

College of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, P. R. China

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An extraction and catalytic oxidation desulfurization (ECODS) system composed of V₂O₅, 30 wt % H₂O₂ and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄) as the basic experiment was used for the removal of DBT from the model oil at moderate temperature (30 °C). In the reaction process, V₂O₅ was oxidized by H₂O₂ into peroxovanadium compounds. Meanwhile, the sulfur-containing compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT), were extracted into ionic liquid (IL) from the model oil and oxidized into their corresponding sulfones by peroxovanadium compounds. The reactivity of sulfur-containing compounds in the ECODS followed this order: DBT > BT > 4,6-DMDBT. In the case of ECODS, the sulfur removal of DBT can reach 98.7%, which was superior to that of the simple extraction with IL (16.5%) or the catalytic oxidation (2.8%). This ECODS system could be recycled seven times without a significant decrease in activity.

Introduction

Transportation fuels are developing so fast because of their advantages of cost-efficiency and big power. However, SO_x is emanated from the combustion of sulfur compounds in gasoline and diesel oil at high temperature, which brings environmental problems. Therefore, many stringent environment legislations have been issued to limit the sulfur content of fuels.^{1,2}

There are two conventional desulfurization methods: hydrosulfurization (HDS) and non-HDS. In the past few years, most of the sulfur was removed from the fuels through HDS. The sulfur-containing compounds left in fuels after HDS are mainly benzothiophene (BT), dibenzothiophene (DBT), and their derivatives. However, taking this method to get the lower sulfur content to meet the environment legislations, it must be operated at a higher temperature under higher hydrogen pressures, which induces high operating cost

and investment. Therefore, many non-HDS approaches have been developed, including: oxidation,^{3–14} extraction,^{15–21} adsorption,^{22–25} and bioprocesses.²⁶ Among these methods, oxidative desulfurization (ODS) combined with extraction is considered to be one of the most promising processes, in which the sulfur compounds can be oxidized into their corresponding sulfoxides and sulfones. Then, the oxidized sulfur compounds are removed by polar extractants in the following process. Some flammable and volatile organic compounds (VOCs) were used as extractants, such as acetonitrile,²⁷ DMSO,²⁸ and DMF,²⁹ which lead to further environmental and safety concerns. Therefore, it is highly desirable to look for suitable extractants to meet the demands of green standards.

*To whom correspondence should be addressed. Telephone: 86-0511-88791800. Fax: 86-0511-88791708. E-mail: lihm@ujs.edu.cn.

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Table 1. Influence of Different Reaction Systems^a

entry	desulfurization system	sulfur removal (%)				no IL
		[Bmim]BF ₄	[Omim]BF ₄	[Bmim]PF ₆	[Omim]PF ₆	
1	IL	16.5	23.8	13.6	26.9	
2	IL + H ₂ O ₂	19.3	25.3	17.1	31.6	
3	IL + H ₂ O ₂ + V ₂ O ₅	98.7	28.9	22.1	70.1	
4	H ₂ O ₂ + V ₂ O ₅					2.8

^a Experimental conditions: model oil = 5 mL, IL = 1 mL, $[n(\text{DBT})/n(\text{V}_2\text{O}_5) = 20]$, $[n(\text{H}_2\text{O}_2)/n(\text{DBT}) = 6]$, $T = 30\text{ }^\circ\text{C}$, $t = 4\text{ h}$.

Room temperature ionic liquids (ILs) have been put in a wide range of application as green solvents for their low-volatility and excellent thermal stability. Currently, desulfurization of diesel fuels using ILs has been reported. However, sulfur removal by mere extraction with the ILs was not high.³⁰ Chemical oxidation in conjunction with IL extraction can increase the removal of sulfur sharply. For instance, Wei³¹ has reported that ODS combined with water-immiscible IL of 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]-PF₆) lead to a high oxidation rate. The oxidation desulfurization of fuels using acidic ionic liquids ([Hmim]BF₄ and [Hnmp]BF₄) with H₂O₂ has been studied by Lu³² and Zhao,⁹ and the sulfur removal of the model oil could reach over 90%. Recently, some reports have presented that the polyoxometalate/H₂O₂/IL for extraction and catalytic oxidation desulfurization (ECODS) exhibits high catalytic activity in the desulfurization by our group.^{4–6,13} In the previous work, tungsten- and molybdenum-containing catalysts were in the ECODS, which can deeply remove DBT from model oil, and catalysts play an important role in desulfurization.

Recently, catalysts supported by vanadium-containing compounds have been widely used in desulfurization.^{33–37} For example, V₂O₅/Al₂O₃, V₂O₅/TiO₂, and V₂O₅/SiO₂–Al₂O₃ were introduced in desulfurization systems, and sulfur removal was investigated. However, few reports have been presented where V₂O₅ was taken as catalyst in the ECODS with IL. Herein a new system combination of V₂O₅, H₂O₂, and IL for ECODS of model oil has been developed. Four ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]-BF₄), 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([Omim]-BF₄), [Bmim]PF₆, and 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([Omim]PF₆), were introduced into the ECODS. In moderate temperature (30 °C), the ECODS system can deeply remove the sulfur compounds in model oil.

Experimental Section

The ionic liquids [Bmim]BF₄, [Bmim]PF₆, [Omim]BF₄, [Omim]PF₆ were purchased from Shanghai Cheng Jie Chemical Co. Ltd. Model oil was prepared by dissolving DBT, BT, and 4,6-DMDBT in *n*-octane to give solutions with sulfur contents of

1000, 250, and 250 ppm, respectively. In the reaction process, the mixture including 5 mL of model oil, 30 wt % H₂O₂, 1 mL of IL, and catalyst was stirred vigorously. After the reaction, the model oil was subjected to GC-FID analysis (internal standard method). A 15 m × 0.32 mm I.D. × 1.0 μm film thickness SE-54 capillary column was used for separation.

Results and Discussion

DBT, BT, and 4,6-DMDBT were the main refractory sulfur-containing compounds that were hard to be got rid of through the primary HDS treatment. In this work, the ECODS system was composed of model oil, H₂O₂, IL, and V₂O₅. DBT and V₂O₅ were chosen to be the representative in the optimized experiments.

Influence of Different Reaction Systems. Three different sulfur removal systems were investigated. Four kinds of ILs were used as extractants for DBT-containing model oil. V₂O₅ combined with H₂O₂ could be dissolved in water-miscible [Bmim]BF₄, which then formed biphasic systems with *n*-octane in which model oil was the upper layer while IL with V₂O₅–H₂O₂ was the lower layer. However, in water-immiscible ILs of [Omim]BF₄, [Bmim]PF₆, and [Omim]PF₆, H₂O₂ existed as a single phase in the triphasic systems in which model oil was the upper layer, IL was the lower layer, and H₂O₂ was between the two.

As shown in Table 1, when mere extraction with [Bmim]BF₄ was taken, the sulfur removal was only 16.5%. Under the same conditions, after the addition of H₂O₂ into the model oil, the sulfur removal reached 19.3%. In the absence of IL, the sulfur removal of V₂O₅–H₂O₂ was only 2.8%. However, when V₂O₅, H₂O₂, and [Bmim]BF₄ were combined together, the sulfur removal increased sharply, reaching 98.7%, which showed that V₂O₅ played a vital role in the system and that the combination of V₂O₅, H₂O₂, and [Bmim]BF₄ was rather helpful to the deep desulfurization. These experiments clearly indicated that the ECODS was superior to mere extraction with IL as well as the extractive oxidation without catalyst or the catalytic oxidation. Similar trends can be found to the other three ILs. However, in the case of [Omim]BF₄, [Bmim]PF₆, and [Omim]PF₆, the sulfur removal was only 28.9, 22.1, and 70.1%, respectively, which were lower than that of [Bmim]BF₄. Due to the partitioning effects, the ECODS system showed better activity in the biphasic system than that in the triphasic system.

Influence of Time and Temperature on the Sulfur Removal. The effect of reaction time (0.5, 1, 2, 3, and 4 h) and temperature (30, 40, and 50 °C) on ECODS containing V₂O₅, H₂O₂, and [Bmim]BF₄ are shown in Figure 1. As can be seen, the sulfur removal under different temperature increased with increasing time. With the combination of extraction and catalytic oxidation, DBT in *n*-octane was extracted into the IL and then oxidized. At the time of 0.5 h, the sulfur removal followed the order 50 °C > 40 °C > 30 °C. However, when the reaction time was prolonged to 1.5 h,

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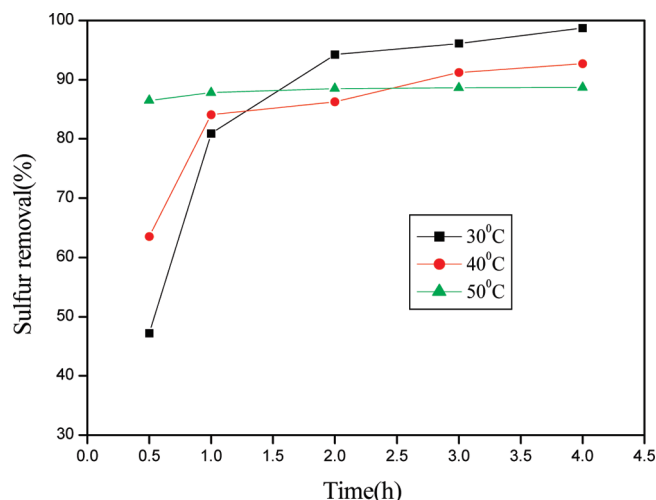


Figure 1. Influence of time and temperature on the sulfur removal. Experimental conditions: model oil = 5 mL, [Bmim]BF₄ = 1 mL, $n(\text{DBT})/n(\text{V}_2\text{O}_5) = 20$, $n(\text{H}_2\text{O}_2)/n(\text{DBT}) = 6$.

Table 2. Influence of the Amount of H₂O₂ on the Sulfur Removal^a

entry	1	2	3	4	5
$n(\text{H}_2\text{O}_2)/n(\text{DBT})$	2:1	3:1	4:1	5:1	6:1
sulfur removal (%)	72.3	89.1	96.7	97.0	98.7

^a Experimental conditions: model oil = 5 mL, [Bmim]BF₄ = 1 mL, $n(\text{DBT})/n(\text{V}_2\text{O}_5) = 20$, $T = 30\text{ }^\circ\text{C}$, $t = 4\text{ h}$.

the sulfur removal of ECODS under 30 °C was better than that under 40 and 50 °C. Meanwhile, the sulfur removal of ECODS under 40 °C was higher than that under 50 °C. It was demonstrated that at the beginning of the reaction (0.5 h), a higher temperature was beneficial for the reaction, whereas with increasing time, the H₂O₂ was decomposed, leading to less sulfur removal. However, under a lower temperature, H₂O₂ can be used more efficiently with less self-decomposition, which induced the high sulfur removal of the entire system, as well as the new order of sulfur removal: 30 °C > 40 °C > 50 °C with time over 2.5 h. According to these data, a lower temperature is more suitable for the V₂O₅–H₂O₂–[Bmim]BF₄–DBT system.

Influence of the Amount of H₂O₂ on the Sulfur Removal.

The effect of the amount of H₂O₂ on the sulfur removal was shown in Table 2. The mixture of H₂O₂ and DBT with 2:1, 3:1, 4:1, 5:1, and 6:1 molar ratios was plotted. When the ratio of $n(\text{H}_2\text{O}_2)/n(\text{DBT})$ was set at 2:1, the sulfur removal was only 72.3%. When the ratio of $n(\text{H}_2\text{O}_2)/n(\text{DBT})$ was 3:1, 4:1, and 5:1, the sulfur removal was 89.1, 96.7, and 97.0%, respectively. When $n(\text{H}_2\text{O}_2)/n(\text{DBT})$ was 6:1, the sulfur removal reached 98.7%, by which the deep desulfurization can be achieved. It is known that $n(\text{H}_2\text{O}_2)/n(\text{DBT})$ should be 2, stoichiometrically, when DBT is oxidized completely. However, a stoichiometrical amount of H₂O₂ cannot give the complete oxidation of DBT in the system due to its self-decomposition. Therefore, with the increasing amount of H₂O₂, the oxidation was put forward well and the sulfur removal increased.

Influence of the Amount of Catalyst on the Sulfur Removal.

The effect of the amount of catalyst on the desulfurization system containing V₂O₅, H₂O₂, and [Bmim]BF₄ was investigated and the results are shown in Table 3. The mixture of DBT and catalyst with 5:1, 10:1, and 20:1 molar ratios has been plotted. As can be seen, when the $n(\text{DBT})/n(\text{catalyst})$ was set at 80:1, 95.4% of the sulfur removal was obtained.

Table 3. Effect of the Amount of Catalyst on the Sulfur Removal^a

entry	1	2	3
$n(\text{DBT})/n(\text{V}_2\text{O}_5)$	80:1	40:1	20:1
Sulfur removal (%)	95.4	96.2	98.7

^a Experimental conditions: model oil = 5 mL, [Bmim]BF₄ = 1 mL, $n(\text{H}_2\text{O}_2)/n(\text{DBT}) = 6$, $T = 30\text{ }^\circ\text{C}$, $t = 4\text{ h}$.

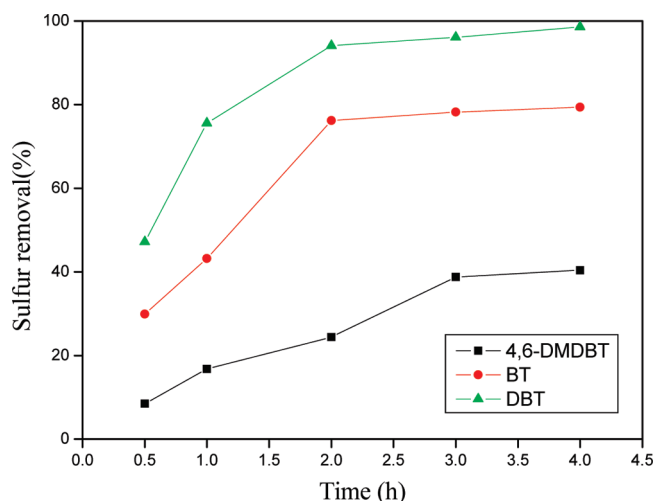


Figure 2. Influence of different substrates in the EDODS system. Experimental conditions: model oil = 5 mL, [Bmim]BF₄ = 1 mL, $n(\text{sulfur})/n(\text{V}_2\text{O}_5) = 20$, $n(\text{H}_2\text{O}_2)/n(\text{sulfur}) = 6$, $T = 30\text{ }^\circ\text{C}$.

When the ratio was fixed at 20:1, the efficiency reached 98.7%. The experimental results showed that the sulfur removal increased with the increasing DBT/catalyst molar ratio.

Influence of Different Substrates in the EDODS System.

The effect of the different substrates on desulfurization in the V₂O₅–H₂O₂–[Bmim]BF₄ system was also investigated, and BT, DBT, and 4,6-DMDBT were taken as the representative sulfur compounds. In Figure 2, the removal of BT, DBT, and 4,6-DMDBT was 29.9, 47.2, and 8.5% at 0.5 h, respectively. However, the sulfur removal of DBT reached 98.7% for 4 h, whereas BT and 4,6-DMDBT could only reach 79.4 and 40.4%, respectively. The removal of sulfur compounds increased with the increasing time. It could be seen that the activities of three sulfur compounds followed as DBT > BT > 4,6-DMDBT. Among the three sulfur compounds, the activity was influenced mainly by two factors, that is, steric hindrance and electron density around the sulfur atom of sulfur compounds. Because 4,6-DMDBT had two methyl groups, as well as the highest steric hindrance, leading to the lowest activity. For DBT and BT, the electron density on the sulfur of DBT (5.758) is higher than that of BT (5.739).³⁸ Higher electron density on the sulfur atom was beneficial for the oxidation of the sulfur atom by H₂O₂. So, the activity of DBT was higher than that of BT. Because of these two factors, the activities of three sulfur compounds in the ECODS system decreased in the order of DBT > BT > 4,6-DMDBT.

Recycle of the ECODS System. The recycle of this system for [Bmim]BF₄ containing V₂O₅ has been investigated. After the first reaction, the ionic liquid phase (under-layer) was distilled in an oil bath at 100 °C for about 2 h, until H₂O₂ was

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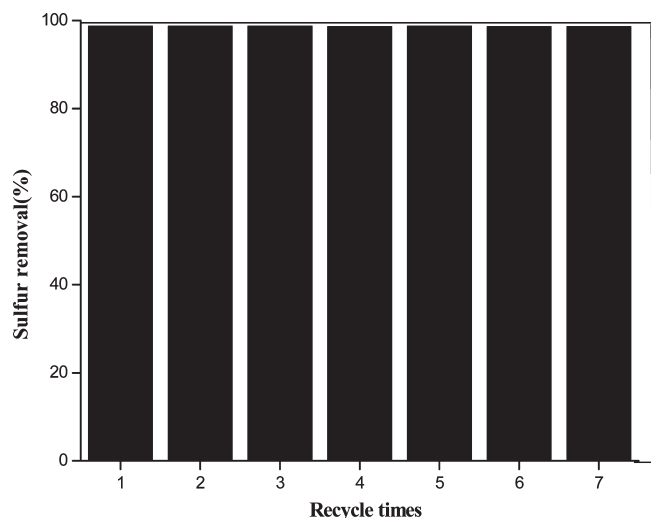


Figure 3. Recycle of the extractive and catalytic system. Experimental conditions: model oil = 5 mL, [Bmim]BF₄ = 1 mL, $[n(\text{DBT})/n(\text{V}_2\text{O}_5) = 20]$, $[n(\text{H}_2\text{O}_2)/n(\text{DBT}) = 6]$, $T = 30\text{ }^\circ\text{C}$, $t = 4\text{ h}$.

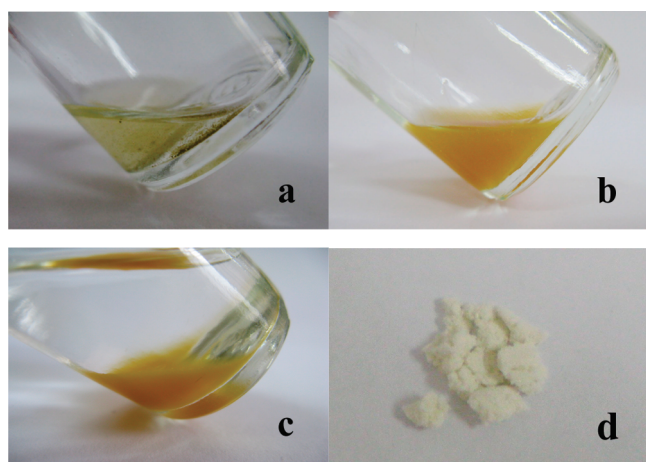


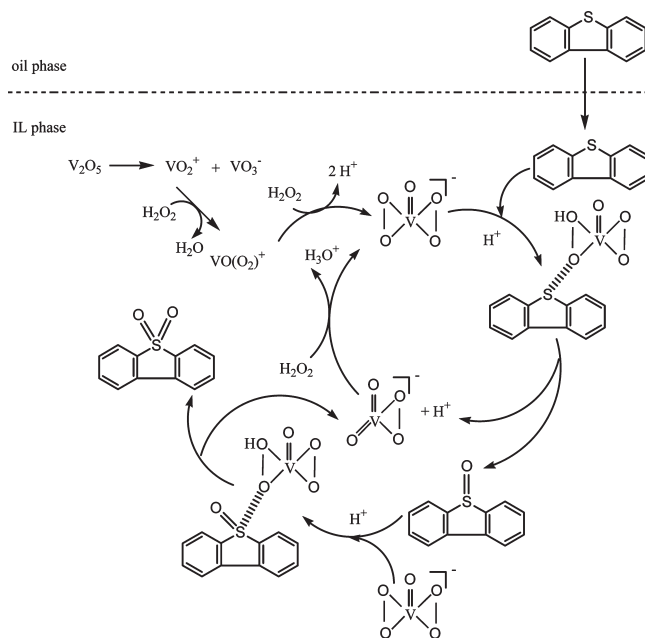
Figure 4. Photos of different desulfurization systems. (a) The system containing V₂O₅ and [Bmim]BF₄. (b) The system containing V₂O₅, [Bmim]BF₄ and H₂O₂. (c) The system containing V₂O₅, [Bmim]BF₄, H₂O₂ and DBT. (d) Reclaimed DBTO₂ by centrifugation.

removed entirely. Then, fresh H₂O₂ and model oil were put into the vaporized ionic liquid phase for the next reaction. According to Figure 3, there was no significant decrease in desulfurization activity of the extractive and catalytic system for [Bmim]BF₄ containing V₂O₅ after seven uses.

The Supposed Process and Mechanism of ECODS System.

DBT was chosen as the sulfur compound to research the mechanism of ECODS. The catalytic oxidation system containing V₂O₅ and H₂O₂ in [Bmim]BF₄ was taken as a research model. To clarify the processes of the ECODS in IL, different photos are listed in Figure 4. The ECODS was composed of V₂O₅, [Bmim]BF₄, 30% H₂O₂, and model oil, which were added into the flask at 30 °C. V₂O₅ was added into [Bmim]BF₄, and the mixture was stirred for about 10 min and allowed to stand for 5 min. V₂O₅ was almost not dissolved in IL (Figure 4a). When H₂O₂ was added, it was

Scheme 1. Supposed Mechanism of the Deep ECODS Using V₂O₅ Catalyst in IL



found that V₂O₅ dissolved in IL and was oxidized to VO(O₂)⁺ and VO(O₂)₂[−].^{39,40} The IL phase turned yellow (Figure 4b). With addition of model oil, a biphasic system formed, in which IL containing V₂O₅ and H₂O₂ was the lower layer while the model oil was the upper layer (Figure 4c). During the reaction, the peroxovanadium compound VO(O₂)₂[−] was the active species in the reaction and transferred active oxygen to the S atom (Scheme 1).^{41,42} VO(O₂)₂[−] is very effective for the oxidation of sulfur compounds (DBT) to sulfoxides and sulfoxide to sulfone. Due to the excess H₂O₂, VO₂(O₂)[−] could be transferred to VO(O₂)₂[−], forming a circulatory system. The white solid (DBTO₂) could be accumulated in the IL phase and separated from IL by centrifugation (Figure 4d). The IR spectrum of the reclaimed white solid matched the IR spectrum of DBTO₂ obtained by Shiraishi.⁴³ In this way, deep desulfurization can be achieved.

Conclusion

The deep desulfurization system including H₂O₂, V₂O₅, and [Bmim]BF₄, under mild conditions, has been proved efficient, and the results are listed as follows: In this work, the ECODS system showed high sulfur removal, which was superior to mere extraction with IL and extractive oxidation without catalyst. For the system of V₂O₅–[Bmim]BF₄–H₂O₂, especially, the optimized condition was suggested: model oil = 5 mL, $T = 30\text{ }^\circ\text{C}$, $t = 4\text{ h}$, $[n(\text{DBT})/n(\text{V}_2\text{O}_5) = 20]$, $[n(\text{H}_2\text{O}_2)/n(\text{DBT}) = 6]$, and IL = 1 mL. The reactivity of sulfur compounds in the ECODS system decreased in the order of DBT > BT > 4,6-DMDBT under the same conditions. The extractive and catalytic system containing V₂O₅ and

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[Bmim]BF₄ can be recycled seven times without a significant decrease in activity. This ECODS system is a simple, mild, and environmentally friendly approach for deep desulfurization.

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