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(12) Patent:

(54) METHOD OF MAKING A SUPERIOR JET FUEL

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1 processing steps is used and wherein the Engler distillation  
2 20% point of the jet fuel product is maintained within a  
3 critical range, a Mach-3 jet fuel can be produced which  
4 meets the desired rigorous specifications when starting  
5 from a virgin crude oil or from a heavy, natural condensate.

6 The present invention involves the processing  
7 sequence of a first distillation to obtain a charge stock  
8 boiling within the range of 355°F. to 510°F., followed by  
9 desulfurization, reforming, extraction, hydrofining, and  
10 adsorption, with the associated distillation steps which are  
11 required in order to obtain a final product boiling within  
12 the range of 375°F. to 495°F. and having an Engler  
13 distillation 20% point of 408°F. minimum and preferably  
14 within the range of about 410°F. to 414°F.

15 Referring now to the drawing, a preferred mode of  
16 the present invention is disclosed as comprising a first step  
17 of fractionating a paraffinic feedstock such as crude oil or  
18 heavy condensates (obtained from distillate wells and the  
19 like) introduced into fractionating tower 101 by way of  
20 line 102. A low-boiling overhead stream is withdrawn by way  
21 of line 103, and a high-boiling stream is removed by way of  
22 line 104, with a heart cut fraction boiling within the range  
23 of 355°F. to 510°F. being obtained by way of line 105. The  
24 heart cut is the charge stream to the processing sequence of  
25 the present invention.

26 The charge stream is admixed with hydrogen supplied  
27 by way of line 106 and is contacted with a hydrodesulfurization  
28 catalyst in the hydrodesulfurization zone 108. A  
29 hydrodesulfurized product is withdrawn by way of line 110  
30 (and may be distilled in a fractionator to obtain a dry point  
31 of the overhead product of 490°F. to 500°F.), admixed with  
32 hydrogen supplied by way of line 112, and subjected to

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1 catalytic reforming in the catalytic reforming zone 114.

2 A reformed product stream is removed by way of  
3 line 116, preferably through a stabilizer tower (not shown),  
4 where the light ends are removed to give an IBP (initial  
5 boiling point) minimum of 300°F., and is then contacted  
6 preferably with sulfur dioxide as a solvent for aromatic  
7 hydrocarbon in the zone 118. In this step the SO<sub>2</sub> is  
8 introduced by way of line 120 and an aromatic extract is  
9 removed by way of line 122, the paraffinic raffinate being  
10 withdrawn by way of line 124. The raffinate is then  
11 fractionated in order to obtain an overhead fraction boiling  
12 below about 500°F., for example having an Engler FBP (final  
13 boiling point) of 480°F. to 490°F. In this distillation step  
14 the heavy polymers which are produced in the reformer 114  
15 and/or the hydrodesulfurizer 108 are removed in the high-  
16 boiling material. For this purpose the raffinate is  
17 introduced into distillation column 130, and a high-boiling  
18 bottoms stream, withdrawn by way of line 132 while the  
19 overhead stream, having an FBP of about 480°F. to 490°F., is  
20 withdrawn by way of line 134.

21 The overhead stream 134 is admixed with hydrogen  
22 supplied by line 136 and introduced into a hydrofining zone  
23 138, wherein the distilled raffinate is hydrofined. The  
24 hydrofined material may be fractionated to adjust the initial  
25 boiling point to about 380°F. and is then introduced into  
26 adsorption zone 142 as a final finishing step. In the  
27 adsorption zone 142, the residual aromatic compounds are  
28 removed and thermal stability of the fuel improved. The  
29 Mach-3 fuel is withdrawn by way of line 144 and may be caustic  
30 washed before or after adsorption if desired. The various  
31 distillation steps after the reforming operation must produce  
32 a final product having an Engler 20% point within the range of

1 410°F. to 414°F. Obviously, this may be accomplished by  
 2 distillation at any of many points in the processing sequence,  
 3 but preferably the 20% point is adjusted in the final  
 4 distillation zone 130 or in a distillation zone (not shown)  
 5 after hydrofining in zone 138. By raising the Engler 20%  
 6 point to 408°F. minimum, preferably 410°F. to 414°F., the  
 7 luminometer number and heat of combustion are maximized while  
 8 the freeze point is minimized, contrary to what would be  
 9 expected. It normally would be expected that these values  
 10 would degrade with an increasing 20% point. However, it has  
 11 been found that with the 20% point within the prescribed 4°F.  
 12 range, the luminometer number, freeze point, and Btu ratings  
 13 of the fuel are at their most desirable values, less desirable  
 14 values for each being obtained at a 20% point either higher or  
 15 lower than the critical range.

16 This is seen from the following Table II, wherein  
 17 the changes of the luminometer number, the freeze point, and  
 18 the heat of combustion are shown.

19 TABLE II

	<u>402°F.</u>	<u>410°F.</u>
20 Luminometer Number	123.0	126.9
21 Freeze Point	-42°F.	-43°F.
22 Heat of Combustion, Btu/lb.	18,936	18,948

24 Thus, it is seen that in order to make the rigorous  
 25 specifications, the Engler 20% point of the product must be  
 26 maintained within the narrowly prescribed range.

27 In general, the processing scheme has been shown to  
 28 include a prefractionation step followed by hydrodesulfurization,  
 29 catalytic reforming, extraction, fractionation, hydrofining,  
 30 and adsorption in order to produce a superior quality Mach-3  
 31 jet fuel. The individual steps, including the variables  
 32 involved therein, are discussed in sequence below.

1 Feedstock

2           The oil to be used as an ultimate feedstock is  
3 obtained from a paraffinic crude such as Panhandle crude or  
4 from field condensates. The preferred crude oil will contain  
5 at least about 40% paraffins and less than about 60%  
6 aromatics plus naphthenes.

7 Distillation

8           The selected crude oil is then distilled in order to  
9 obtain a distillate having a boiling range from about 355°F.  
10 to about 510°F. containing from about 30 to about 50% normal  
11 paraffins, from about 10 to about 40% isoparaffins, from about  
12 40 to about 60% aromatics plus naphthenes, and from about 0  
13 to about 5% olefins. The fractionation step removes high  
14 boiling, unsuitable materials from the fuel.

15 Desulfurization

16           The distilled fraction is submitted to  
17 hydrodesulfurization, wherein the fraction is contacted with a  
18 hydrodesulfurizing catalyst such as extruded or pilled cobalt  
19 molybdate. The temperature in the hydrodesulfurization zone  
20 suitably may range from about 600°F. to about 690°F., the  
21 pressure from 150 psig to 300 psig, and a hydrogen feed rate  
22 from 200 scf/bbl. to 600 scf/bbl. of feed, based on pure  
23 hydrogen. The hydrogen recycle stream containing from about  
24 60% to about 95% hydrogen may be used, in which case the  
25 amount of hydrogen recycle stream per barrel of feed will be  
26 larger than would be the case if pure hydrogen were being used.

27           The charge to the hydrodesulfurizing zone shall  
28 suitably involve a space velocity of from about 2.0 to about  
29 4.0 volumes of hydrocarbon feed per volume of catalyst per hour.

30           In the hydrodesulfurizing step, the sulfur is removed  
31 and the sulfur content of the material is reduced from about  
32 0.10 to 0.25% in the feed to about 0.002 to about 0.009% sulfur

1 in the effluent from the hydrodesulfurization unit. The H<sub>2</sub>S  
2 and low-boiling materials produced by hydrodesulfurization  
3 may be removed by steam stripping in order to provide a more  
4 suitable feedstock for the following reforming step.

#### 5 Catalytic Reforming

6 The hydrodesulfurized stream is then charged into  
7 the reforming zone and contacted with hydrogen in the presence  
8 of a reforming catalyst such as platinum on alumina, which has  
9 both aromatizing and isomerizing activity. The temperature  
10 may range from about 825°F. to about 900°F.; the pressure from  
11 150 psig to 450 psig; the amount of hydrogen to hydrocarbon  
12 feed from 2000 scf per barrel to 7000 scf per barrel (based  
13 on pure hydrogen); and the space velocity may be from 0.2 to  
14 2.0 V/V/Hr.

15 In the reforming zone, the naphthenic hydrocarbons  
16 are preferentially converted into aromatic hydrocarbons, which  
17 makes them susceptible to extraction. It is essential to  
18 operate the reformer at a minimum temperature of 825°F. to  
19 permit isomerization of normal to isoparaffins. While the  
20 ratio of iso- to normal paraffins in the feed may be as low  
21 as 0.2 to 0.5, the ratio in the finished product must be in  
22 the order of 2.0. The preceding hydrodesulfurizing step  
23 prepares the material for reforming by removing sulfur, which  
24 would interfere with the activity of the catalyst in this  
25 preferential isomerization-aromatization reaction.

#### 26 Extraction

27 The reformed stream is then passed into preferably  
28 an SO<sub>2</sub> extraction zone wherein the extraction is carried out.  
29 For SO<sub>2</sub>, the extraction must be carried out under critical  
30 conditions in order to minimize the amount of aromatics  
31 remaining in the raffinate stream. The maximum temperature  
32 in the extraction tower may range from about 50°F. to about

1 100°F., but is preferably maintained at about 65°F. A  
2 temperature gradient in the extraction tower of from about  
3 40°F. to about 100°F. may be used, while a solvent-to-  
4 hydrocarbon ratio within the range from about 9:10 to about  
5 2:1 volumes of solvent per volume of hydrogen may be used.  
6 By practicing the extraction step with sulfur dioxide under  
7 these conditions, a raffinate may be obtained which contains  
8 less than 3% aromatic hydrocarbon. Ammonia and phenol may be  
9 used instead of SO<sub>2</sub> extraction, but the same general  
10 temperature limits will apply.

#### 11 Distillation

12 The raffinate is then submitted to after-  
13 fractionation in order to remove polymeric high-boiling  
14 materials formed in the hydrodesulfurization and/or reforming  
15 steps, that is, those hydrocarbons which boil above about  
16 480°F. to 500°F. This high-boiling material is deleterious  
17 because directionally it has an adverse effect on freeze  
18 point, heat content and luminometer number. It is also  
19 likely to reduce thermal stability.

20 The material boiling below 480°F. to 500°F. is then  
21 removed as a product suitable for the finishing steps.

#### 22 Hydrofining

23 The fractionated hydrocarbon is then passed to a  
24 hydrofining unit where it is contacted with hydrogen and a  
25 hydrofining catalyst such as extruded or pilled cobalt  
26 molybdate. The hydrofining step reduces the olefinic content  
27 and removes sulfur, nitrogen and polar compounds. This step  
28 is carried out at a temperature within the range from about  
29 575°F. to about 650°F., a pressure of 250 to 350 psig, a  
30 liquid hydrocarbon space velocity of 1.0 to 4.0 volumes of  
31 hydrocarbon per volume of catalyst per hour, and a hydrogen-  
32 to-hydrocarbon feed ratio of 500 to 1500 scf/bbl. (based on



1 pure hydrogen). The hydrofined hydrocarbon is essentially  
2 free of olefins and aromatics, but may still contain trace  
3 amounts of each component.

#### 4 Adsorption

5 The hydrofined fuel is then passed over an adsorbent  
6 bed having an affinity for polar compounds, such as activated  
7 charcoal, at a treat ratio of 0.5 to 4.0 V/V/Hr., whereby a  
8 thermally stable jet fuel boiling within the range of about  
9 400°F. to 500°F. is obtained, having a heat of combustion of  
10 at least 18,900 Btu/lb., and otherwise meeting the  
11 specifications above set forth. A preferred treat rate is 1.5  
12 to 3.5 V/V/Hr. The adsorption step removes traces of polar  
13 compounds from the fuel.

14 As an example of the present invention, a run  
15 utilizing Panhandle crude was made, and the processing  
16 sequence above set forth was generally followed. A crude  
17 fraction boiling within the range of 355°F. to 510°F. was  
18 submitted to hydrodesulfurization. The sulfur content was  
19 reduced from 1400 ppm to about 50 ppm by contacting the stream  
20 with 260 scf per barrel of hydrogen over a cobalt molybdate  
21 catalyst at 658°F. and 255 psig.

22 The hydrodesulfurized product was catalytically  
23 reformed over a platinum-on-alumina catalyst at 825°F. and  
24 270 psig in the presence of 3200 scf per barrel of hydrogen  
25 and at a space velocity of 0.4 V/V/Hr.

26 The feed rate was 0.4 V/V/Hr. with the reactor  
27 inlet temperature 825°F. with an 85°F. temperature drop across  
28 the reactor. The hydrogen rate was 3500 scf per barrel of  
29 feed, with a pressure of 280 psig. Conversion of naphthenes  
30 to aromatics was approximately 60% to 75% complete, with  
31 liquid yield being over 95%. The ratio of iso- to normal  
32 paraffins in the product exceeded 2.0.

1           The reformat was then charged to an SO<sub>2</sub> extraction  
2 unit at a feed rate of 3200 barrels per day, to provide an SO<sub>2</sub>  
3 treat of 180%. The temperature at the bottom of the mixer  
4 tower was 15°F. to 25°F., while that at the tower top was 65°F.  
5 The aromatics content of the raffinate obtained under these  
6 conditions was indicated to be essentially 0%. The accuracy  
7 of the testing method indicated that less than 0.5% aromatics  
8 remained.

9           The SO<sub>2</sub> raffinate was then caustic washed with 0.02  
10 pound of NaOH per barrel of raffinate, to 0.10 pound per  
11 barrel. The caustic washed material was hydrofined over  
12 cobalt molybdate catalyst at 615°F. to 625°F. and 300 psig  
13 pressure in order to saturate the 0.5 to 1% of olefins which  
14 remained in the fuel. The front end was adjusted by  
15 fractionation at the hydrofining unit.

16           The hydrofined fuel was then caustic washed with  
17 30° Baumé NaOH, and passed over an activated charcoal bed at  
18 about 3 V/V/Hr. in order to maximize thermal stability. The  
19 product obtained is a fuel which boils within the range of  
20 375°F. to 495°F. and has an Engler 20% point of about 410°F.  
21 The fuel meets all specifications of the Mach-3 jet fuel.

22           An analysis of the product is set forth below in  
23 Table III.

1

TABLE III

2	Gravity, °API	52.5
3	Distillation, ASTM	
4	IBP, °F.	395
5	FPB	489
6	5%	404
7	10%	406
8	20%	411
9	30%	416
10	40%	421
11	50%	427
12	60%	433
13	70%	440
14	80%	450
15	90%	465
16	95%	480
17	Luminometer Number	117
18	Freeze Point, °F.	-46
19	Heat content, Btu/lb. net	18,919
20	Aromatics, Vol. %	0.8
21	Isoparaffins	59.8
22	Normal paraffins	28.0
23	Naphthenes	11.4

24                   It was thus seen that Applicants have provided a  
 25 novel combination of processing steps which leads to the  
 26 production of a highly useful supersonic jet fuel. The  
 27 various steps must be accomplished in the order given, with  
 28 the exception of the distillation step after extraction,  
 29 which may be accomplished either before hydrofining or after  
 30 hydrofining, but before adsorption over a polar adsorbent.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process of making a jet fuel which comprises:
  - fractionating a virgin paraffinic hydrocarbon stream to obtain a charge stream boiling within the range of 355°F. to 510°F.;
  - contacting said charge stream with hydrogen and a hydrodesulfurization catalyst under hydrodesulfurization conditions to obtain a desulfurized stream containing less than 0.01% sulfur by weight;
  - contacting said desulfurized stream with hydrogen and a reforming catalyst at a temperature from 825°F. to 900°F., a pressure from 150 psig to 450 psig, and a space velocity from 0.2 to 2.0 V/V/Hr., whereby naphthene aromatization and normal paraffin isomerization are maximized in obtaining a reformed stream;
  - extracting substantially all of the aromatic hydrocarbons from said reformed stream by contact with a solvent for aromatic hydrocarbons to obtain a raffinate containing less than 3% aromatic hydrocarbons;
  - hydrofining said raffinate by contact with hydrogen and a hydrofining catalyst under hydrofining conditions to obtain a hydrofined product; and
  - contacting said hydrofined product with an adsorbent for polar compounds to obtain a thermally stable jet fuel;
  - said jet fuel being subjected to at least one fractionation step during the course of said process whereby the Engler distillation 20% point thereof is 408°F. minimum, and the fuel boils within the range of 375°F. to 495°F.
2. A process in accordance with claim 1 wherein the hydrodesulfurization catalyst is cobalt molybdate, and said hydrodesulfurization conditions comprise a temperature within the range of 600°F. to 690°F., a pressure within the range from 150 psig to 300 psig, and a space velocity of 2 to 4 V/V/Hr.

3. A process in accordance with claim 1 wherein said reforming catalyst is platinum on alumina.

4. A process in accordance with claim 1 wherein the solvent for aromatic hydrocarbons is chosen from the group consisting of  $\text{SO}_2$ ,  $\text{NH}_3$ , and phenol.

5. A process in accordance with claim 1 wherein the solvent for aromatic hydrocarbons is  $\text{SO}_2$ , and the extraction is accomplished at a solvent-to-hydrocarbon ratio from 9:10 to 2:1 in an extraction zone at a maximum temperature from  $50^\circ\text{F}$ . to  $100^\circ\text{F}$ . and a maximum temperature gradient across said zone from  $40^\circ\text{F}$ . to  $100^\circ\text{F}$ .

6. A method in accordance with claim 2 wherein the reforming catalyst is platinum on alumina.

7. A method as in claim 6 wherein the solvent for aromatic hydrocarbons is  $\text{SO}_2$ , and the extraction is accomplished at a solvent-to-hydrocarbon ratio of from 9:10 to 2:1 in an extraction zone at a maximum temperature from  $50^\circ\text{F}$ . to  $100^\circ\text{F}$ . and a maximum temperature gradient across said zone from  $40^\circ\text{F}$ . to  $100^\circ\text{F}$ .

8. A method as in claim 6 wherein the hydrofining catalyst is cobalt molybdate, and said hydrofining conditions comprise a temperature from  $575^\circ\text{F}$ . to  $650^\circ\text{F}$ ., a pressure from 250 psig to 350 psig, a space velocity from 1.0 to 4.0 V/V/Hr., and a hydrogen-to-hydrocarbon ratio from 500 to 1500 scf/bbl.

9. A process of making a jet fuel which comprises:  
fractionating a hydrocarbon stream to obtain a charge stream boiling within the range of  $355^\circ\text{F}$ . to  $510^\circ\text{F}$ . and comprising from 30 to 50% normal paraffins, from 10 to 40% isoparaffins, from 40 to 60% aromatic and naphthenic hydrocarbons, and from 0 to 5% olefins;

contacting said charge stream with from 200 to 600 scf of hydrogen per barrel of charge stream in the presence of a cobalt molybdate hydrodesulfurization catalyst, at a temperature from 600°F. to 690°F., a pressure of 150 psig to 300 psig, and a space velocity of 2 to 4 V/V/Hr., whereby there is obtained a desulfurized stream containing less than 0.01% sulfur;

contacting said desulfurized stream with from 2000 to 7000 scf of hydrogen per barrel of desulfurized stream in the presence of platinum on alumina reforming catalyst, at a temperature from 825°F. to 900°F., a pressure from 150 psig to 450 psig, and a space velocity from 0.2 to 2.0 V/V/Hr., whereby naphthene aromatization and normal paraffin isomerization are maximized in obtaining a reformed stream;

extracting substantially all of the aromatic hydrocarbons from said reformed stream by contact with from 0.9 to 2.0 volumes of SO<sub>2</sub> per volume of reformed stream in an extraction zone at a maximum temperature from 50°F. to 100°F. and a temperature gradient across said zone of 40°F. to 100°F., whereby there is obtained a raffinate containing less than 3% aromatic hydrocarbons;

fractionating said raffinate to obtain a raffinate fraction boiling below 480°F.;

hydrofining said raffinate fraction by contact with a cobalt molybdate hydrofining catalyst and from 500 to 1500 scf of hydrogen per barrel of raffinate fraction at a temperature from 575°F. to 650°F., a pressure from 250 psig to 350 psig, and a liquid hydrocarbon space velocity of 1.0 to 4.0 V/V/Hr., whereby an essentially olefin- and aromatic hydrocarbon-free hydrofined product is obtained;

fractionating said hydrofined product to obtain a hydrofined fraction boiling below 480°F. and having an Engler distillation 20% point of 410°F. to 414°F.; and

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contacting said hydrofined fraction with activated charcoal at a space velocity of 0.5 to 4.0 V/V/Hr.,

whereby there is obtained a jet fuel having a luminometer number of at least 100, a heat of combustion of at least 18,900 Btu/lb., a maximum viscosity at -30°F. of 15 centistokes, and a maximum freezing point of -40°F.



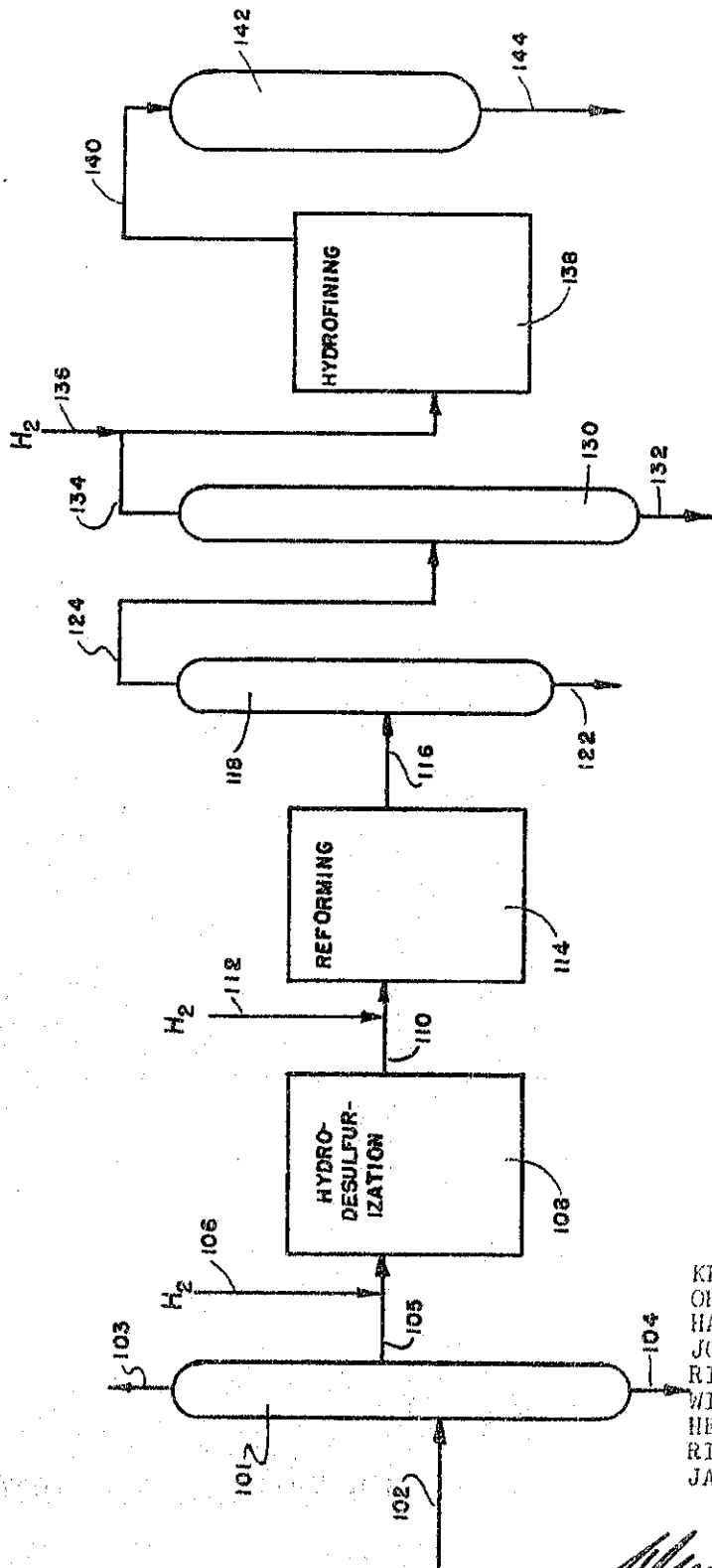


FIG. 1

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