

[54] **RECOVERY OF ORGANIC MATTER FROM
ORGANIC MINERAL-CONTAINING
DEPOSITS**

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1973.

[52] U.S. Cl. **166/303; 208/11**

[51] Int. Cl.² **E21B 43/24**

[58] Field of Search 299/4, 5, 3; 166/272, 302,
166/303, 311, 312; 208/11

[56] **References Cited**

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[57]

ABSTRACT

Organic matter, including valuable hydrocarbons, are recovered from organic mineral-containing deposits such as oil shale, tar sands, etc., by treating them with molecular sulfur and an extraction fluid, e.g., benzene, at temperatures ranging from about 200° to about 1000°F.

9 Claims, 5 Drawing Figures

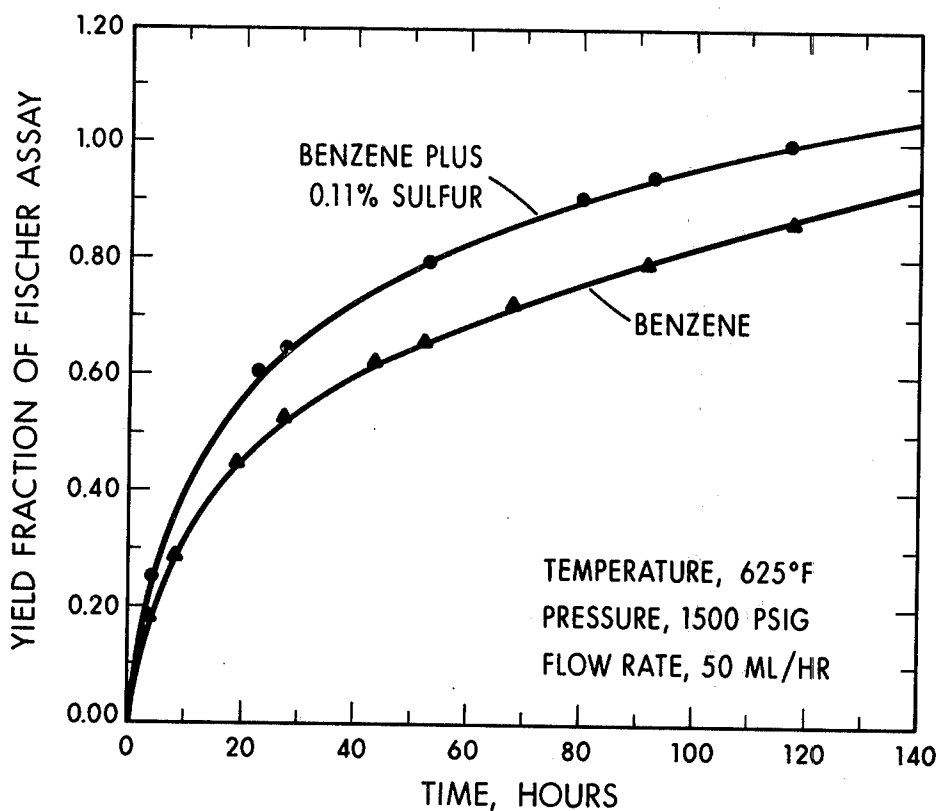


Figure 1. Extraction of oil shale with benzene and sulfur.

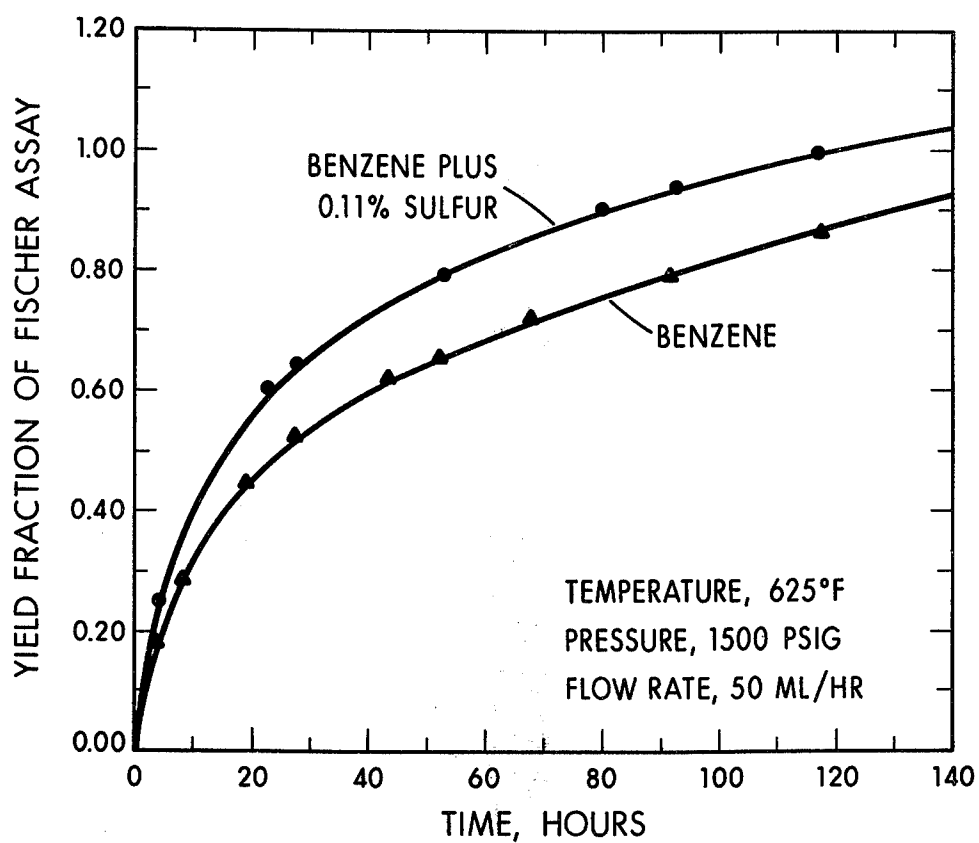


Figure 1. Extraction of oil shale with benzene and sulfur.

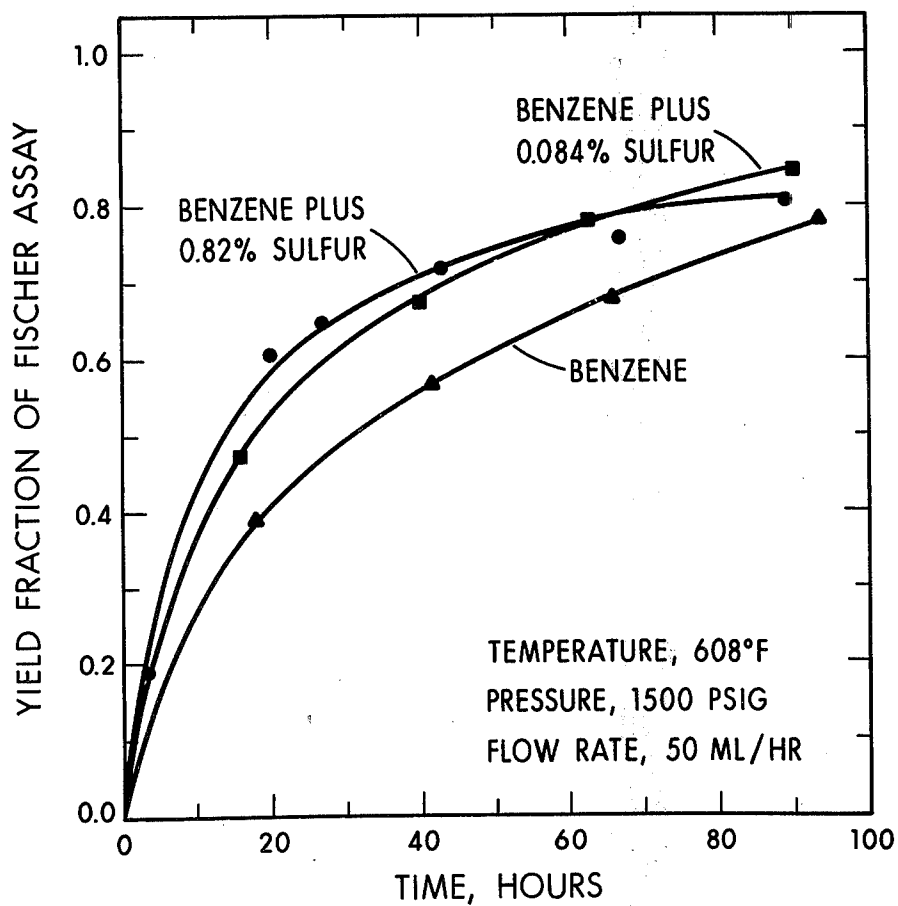


Figure 2. Extraction of oil shale with benzene and sulfur.

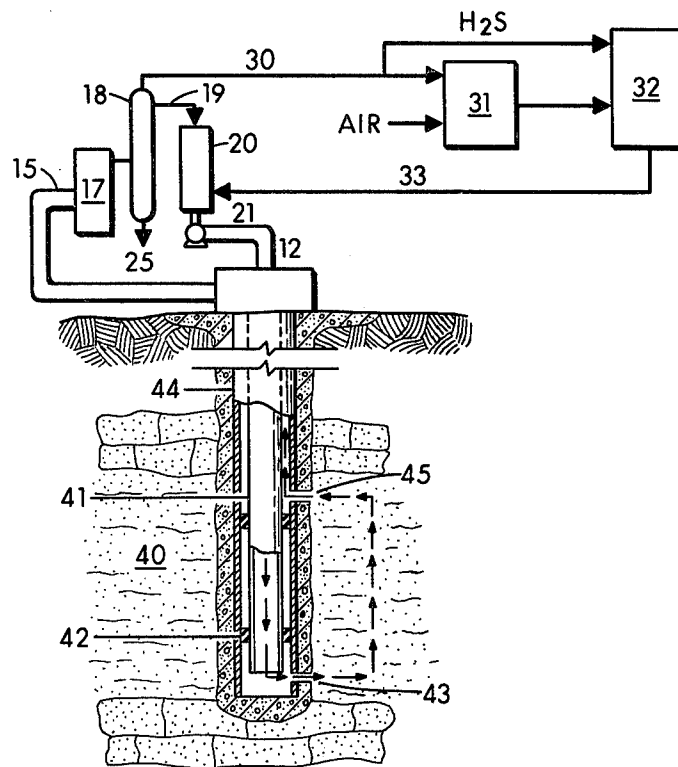


Figure 3. In situ extraction of shale oil.

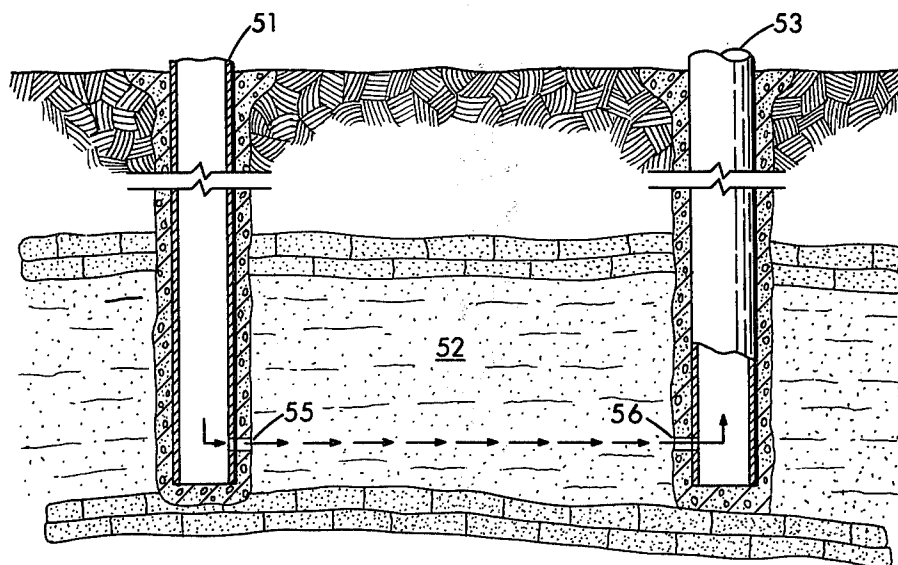


Figure 4. In situ extraction of shale oil.

RECOVERY OF ORGANIC MATTER FROM ORGANIC MINERAL-CONTAINING DEPOSITS

This application is a continuation-in-part of our co-pending U.S. Pat. application Ser. No. 380,783, filed Aug. 9, 1973.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the general area of recovery of the organic matter from organic mineral-containing deposits found in subterranean formations.

2. Description of the Prior Art

U.S. Pat. Nos. 3,527,692 and 3,474,863 have taught the recovery of hydrocarbons from oil shale by treatment with a sulfur-containing compound, i.e., hydrogen sulfide, in the presence of an extraction fluid. The sulfur employed in these inventions is in the -2 oxidation state [S^{-2}]. The present invention employs sulfur in the zero oxidation state [S^0]. The latter is capable of undergoing redox reactions with the organic and inorganic matter in the organic mineral-containing deposit, e.g., oil shale, thereby accelerating the rate of oil recovery.

SUMMARY OF THE INVENTION

General Statement of the Invention

According to the present invention, organic matter is recovered from organic mineral-containing deposits, e.g., oil shale, by contacting oil shale with elemental sulfur, [S^0], and an extraction fluid at temperatures in the range of from about 200° to about $1,000^{\circ}\text{F}$. Ideally, the extraction fluids should not react substantially with the elemental sulfur.

The invention may be practiced above ground after first mining the organic mineral-containing matter from a subterranean deposit, or more preferably, "in situ" by injecting the extraction fluid and elemental sulfur into the organic mineral-containing deposit. The injection of elemental sulfur along with the extraction fluid results in increased extraction rates of the organic matter as compared to the corresponding extraction rate with the same extraction fluid in the absence of sulfur.

Utility of the Invention

The present invention is useful for the recovery of organic matter, including valuable hydrocarbons, from naturally occurring organic mineral-containing deposits.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 each graphically depict the extraction of shale oil with benzene and sulfur according to the present invention.

FIG. 3 shows the use of a single well recovery system for the in-situ extraction of the shale oil.

FIG. 4 schematically shows the in-situ extraction of shale oil from a formation using a two well system.

FIG. 5 schematically shows the in-situ extraction of shale oil from a cavity created in an oil shale formation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Organic and Mineral-Containing Natural Deposit

The present invention is useful for the recovery of hydrocarbons from naturally occurring organic miner-

al-containing deposits, including tar sands, oil shale, lignite, torbanite, coorongite, kukersite, etc.

Extraction Fluids

Extraction fluids useful in the present invention are organic or inorganic compounds or mixtures thereof which will dissolve substantial amounts of extracted shale oil without entering into substantial reaction with either the elemental sulfur or the hydrogen sulfide produced in the reaction. A partial list of the type of compounds useful as extraction fluids in the present invention is as follows:

1. Aliphatic hydrocarbons, e.g., methane, hexane, dodecane, isooctane, etc.
2. Aromatic hydrocarbons, e.g., benzene, naphthalene, tert-butylbenzene, etc.
3. Halogenated organic compounds, e.g., chlorobenzene, dichlorobenzene, bromonaphthalene, dodecylchloride, etc.
4. Heterocyclic compounds, e.g., pyridine, quinoline, thiophene, benzothiophene, etc.
5. Ethers, e.g., diphenyl ether, anisole, polyethylene oxide, etc.
6. Amines, e.g. triethylamine, triphenylamine, aniline, etc.
7. Nitrated organic compounds, e.g., nitrobenzene.
8. Inorganic compounds, e.g., water (steam).
9. Various petroleum products, e.g., kerosine, fuel oil, gas oil, whole crude oil, etc.
10. Various cuts from the fractional distillations of shale oil or whole shale oil.
11. Sulfur-containing compounds, e.g., dimethylsulfide, diphenyl sulfone, dibutylsulfide, etc.
12. Combinations of the above-mentioned compounds.

Sulfur

Sulfur employed with the present invention will preferably be of common commercial purity or may be "as mined" since impurities will not normally be of serious consequence and can readily be separated by conventional processing of the recovered shale oil. For best results, the sulfur will preferably be comminuted to promote dissolving.

Temperature

Though not narrowly critical, the temperature of the extraction fluid when it contacts the oil shale or other organic mineral-containing deposit should be in the general range of from 150°F to about $1,000^{\circ}\text{F}$, more preferably from 200°F to about 900°F , and most preferably from 300°F to about 800°F .

Pressure

The pressure employed in the present extraction process ranges from atmospheric pressure to 20,000 psig. In an "in situ" extraction, the pressures on the extraction fluid are preferably sufficient to maintain it in a liquid phase in the reactor or subterranean formation; however, the ideal temperature ranges necessary to maintain high extraction rates are often above the critical temperature of the extraction fluid. As a result, no amount of pressure would produce a liquid phase. In cases where the extraction fluid is above its critical temperature, pressure is controlled to change the density of the critical fluid which in turn governs the heat capacity and extractive properties of the extraction fluid.

Extraction Time

The contact time between the extraction fluid and the organic mineral containing deposit is not narrowly critical but will generally be in the range of from about

0.01 to about 1,000, more preferably from 0.1 to about 500, and most preferably from 1 to about 250 hours.

The present invention can be employed in continuous or batch operations. Furthermore, in continuous operation, the same well can serve as both the injection well and withdrawal well so that the quantity of extraction fluid-elemental sulfur mixture is first injected then allowed to contact the organic mineral-containing deposit for a sufficient time and the recovered organic matter then withdrawn through the same well.

Extraction Apparatus

The experimental extractions are carried out in a high-pressure autoclave into which the extraction fluid is pumped upflow through a bed of oil shale. Pressure on the system is maintained by a backpressure relief valve. The shale oil extract is collected in high-pressure cylinders which can be isolated from the extraction system, depressurized, and the shale oil-extraction fluid mixture collected.

Procedure

The reactor is filled with a known amount of pre-assayed oil shale in either lump or core form. Under the desired operating pressure, 300 ml of extraction fluid is charged to liquid fill the reactor. The flow rate through the reactor is then adjusted and the reactor heated rapidly to the desired extraction temperature. When sulfur is used, it is dissolved in the extraction fluid and pumped along with the latter to the reactor.

When the reactor reaches the desired temperature, the product reservoir is drained. The oil recovered during warmup is not used in the subsequent yield calculations. The initial time of the reaction, i.e., zero time, is taken the moment the extraction unit reaches the desired temperature. Subsequent time measurements are also taken from this reference point. Samples are then taken periodically and the oil yield determined.

The shale oil yields are determined by first filtering or centrifuging the shale oil-extraction fluid mixture to remove the small amount of insoluble matter carried along in the extractate. The extract is then distilled to separate the extraction fluid from the shale oil. The shale oil is subsequently vacuum dried to a constant weight to ascertain the yield. When sulfur is used to promote the extraction, some unreacted molecular sulfur is carried over into the product. To compensate for this, each shale oil sample is analyzed for sulfur. The shale oil yields are then reported on a sulfur-free basis.

EXAMPLE I

The extraction apparatus is filled with lump-size oil shale ($-1/2$ to $+10$ mesh) and extracted with benzene at 625°F and 1,500 psig. The oil shale had a Fischer assay of 33.4 gal/ton (12.45 weight percent oil). The results are shown in FIG. 1.

EXAMPLE II

The extraction apparatus was filled with the same oil shale described in Example I. The extraction was then carried out at the same temperature and pressure stated in Example I; the benzene, however, contained 0.11 percent sulfur. The results are also shown in FIG. 1.

EXAMPLE III

The extraction apparatus was filled with the same oil shale described in Example I and extracted with benzene at 608°F . The results are shown in FIG. 2.

EXAMPLE IV

The extraction apparatus was filled with the same oil shale described in Example I and extracted with benzene containing 0.084 percent sulfur at 608°F .

EXAMPLE V

The extraction apparatus was filled with the same oil shale described in Example I and extracted with benzene containing 0.82 percent sulfur at 608°F .

EXAMPLE VI

Referring to FIG. 3, an extraction fluid containing sulfur is injected through inner well pipe 41 at a temperature of about 600°F to the bottom of the well where a packer 42 causes it to exit through a perforation 43 into an oil shale formation 40 which has previously been fractured by conventional techniques, e.g., explosive fracturing, leaching of sodium-containing minerals, mining, mining and explosive rubblelizing, etc., in order to render the formation permeable to the flow of fluids. The hot extraction fluid, together with extracted shale oil removed from the formation enter the annular well pipe 44 through a second, higher, perforation 45. The mixture flows upward to the surface and into pipe 15, and then into settling tank 17 to remove the inorganic residue. Centrifuges or filters may be used in the place of or in addition to the settling tank. From the settling tank the extractate is transferred to the fractionator 18 from which a bottoms fraction 25 of shale oil is withdrawn for refinery processing. An overhead of H_2S 30 is withdrawn from the top of the fractionating tower 18, oxidized to SO_2 in burner 31 to which air is fed, and then fed together with another portion of H_2S to reactor 32 in which the H_2S and SO_2 react to form elemental sulfur for recycle through line 33. Fractionation tower 18 also separates the extraction fluid used in the process and recycles it to line 33 through line 19 where it is recombined with sulfur in tank 20. Pump 21 then injects this benzene-sulfur mixture after heating, back into inner pipe 41, repeating the process.

EXAMPLE VII

FIG. 4 shows, schematically, an injection well 51 penetrating a permeable formation 52 which is also penetrated by a production well 53. In a process analogous to that described in Example I, an extraction fluid-sulfur mixture is injected into well 51, moves into a permeable zone, established by fracturing, leaching of a soluble sodium-containing salt, or other methods through perforation 55, and subsequently enters production well 53 through suitable perforations. The output from production well 53 is then treated according to the techniques described in Example VI and the recovered extraction fluid and sulfur are recycled.

EXAMPLE VIII

Referring to FIG. 5, a cavity 10 has been created by a nuclear blast, conventional explosive, a combination of both mining and a conventional explosive, or by fracturing. Alternatively, a drift or adit may be mined into the face of a cliff to establish the cavity and com-

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munication established between the adit and the surface of the cliff where the extraction fluid processing equipment is located. Still another way of establishing the permeability is to simply connect two adits by a horizontal drift. The cavity may or may not be filled with rubble, 11. A hot extraction fluid containing elemental sulfur is pumped downward through injection pipe 12 forming a layer 13 on top of the fine silt-like material 14 at the bottom of the cavity. An extraction fluid-oil shale mixture is withdrawn through induction tube 15 located on the other side of the cavity from injection tube 12. Both tubes have means for gradually raising the level at which they communicate with the cavity in order to maintain their communication above the level of silt in the cavity. AS the extraction proceeds, the oil shale decomposes largely to silt and fills the cavity. Pump 16 located downhole removes the solvent-hydrocarbon mixture. The withdrawn liquids are processes as described in Example VI.

Modifications of the Invention

Variations on the invention, obvious to those skilled in the art, are to be included within the scope of the invention as claimed.

What is claimed is:

1. A process for the recovery of organic matter from organic mineral-containing deposits selected from the groups consisting of tar sands, oil shale, lignite, torbanite, coorongite and kukersite, by contacting the organic mineral-containing deposits at a temperature of from about 200 to about 1000°F with an extraction fluid and elemental sulfur, said elemental sulfur being

6

present in the range of from about 0.001 to about 0.5 parts by weight of sulfur per part by weight of extraction fluid.

2. The process according to claim 1 wherein the contact time between said organic mineral containing deposit and said extraction fluid and elemental sulfur is in the range of from about 0.01 to about 2000 hours.

3. The process according to claim 1 wherein the pressure is maintained in the range of zero to 5000 psig.

4. The process according to claim 1 wherein the extraction fluid is contacted with the organic mineral-containing deposit at temperatures above its critical temperature.

5. The process according to claim 1 wherein the extraction fluid is selected from the group consisting of aliphatic hydrocarbons, aromatic compounds, halogenated organic compounds, heterocyclic organic compounds, organic ether compounds, organic nitrogen-containing compounds, petroleum refinery products, and organic sulfur-containing compounds and mixtures thereof.

6. The process according to claim 1 wherein the extraction fluid comprises at least one cut from the fractional distillation of shale oil.

7. The process according to claim 1 wherein the extraction fluid is water.

8. A process according to claim 1 wherein the organic matter comprises hydrocarbons.

9. A process according to claim 8 wherein the organic mineral-containing deposits comprise oil shale.

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