RECOVERY OF METALS FROM CARBONACEOUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

A process for recovering metals from coal and/or hydrocarbonaceous coke. Particular metals are nickel and vanadium, being found in the greatest concentration in coal and petroleum crude oils; these are recovered in a readily marketable form as nickel oxide and vanadium pentoxide. Salt, preferably sodium chloride, is admixed with coke and the coke is burned at temperatures which allow the salt and metals to fuse to nickel chloride and sodium vanadate. Subsequent treatments result in substantially pure nickel oxide and vanadium pentoxide products. Where the source of the metals in a petroleum crude oil, or heavy hydrocarbonaceous fraction derived therefrom, the salt resulting from an initial desalting operation is utilized within the metals recovery process.

APPLICABILITY OF INVENTION

The inventive concept, embraced by the process herein described is specifically directed toward the recovery of nickel and vanadium from solid carbonaceous material including coal and hydrocarbonaceous coke. In one of its embodiments, hereinafter set forth in greater detail, the present invention relates to a novel method for recovering nickel and vanadium from petroleum crude oil and the heavier hydrocarbon fractions which may be derived therefrom.

Petroleum crude oils, and topped and reduced crude oils, as well as various hydrocarbon fractions and/or distillates, including atmospheric tower bottoms products, vacuum tower bottoms products, crude oil residuum, oils extracted from tar sands, coal oil extract, etc., are generally contaminated by the presence therein of excessive concentrations of various non-metallic and metallic impurities. Among the non-metallic impurities are nitrogen, sulfur, and oxygen, which normally exist as hetero-atomic compounds in relatively large quantities. Of the metallic contaminants, those containing nickel and vanadium are most prevalent, although other metals including iron, copper, lead, zinc, etc., are often present. While the metallic contaminants may exist as suspended metal oxides or sulfides, or water-soluble salts, they are generally found in the form of thermally stable organo-metallic complexes such as metallic porphyrins and various derivatives thereof. Similarly, metals, particularly nickel and vanadium, sulfur, nitrogen and oxygen are known to exist in coal as extremely high molecular weight complexes. With respect to petroleum crude oils, the organo-metallic complexes are linked with sulfur within the pentane-insoluble asphaltene fraction, and become concentrated in the residual portion of the hydrocarbon charge stock.

The high molecular weight asphaltene compounds, with which the organo-metallics are combined, are non-distillable, oil-insoluble coke precursors generally dispersed within a crude oil. When subjected to elevated temperature, as in a vacuum distillation process, the asphaltene have the tendency to flocculate and polymerize, thereby making their conversion to more valuable oil-soluble products extremely difficult. The desirability of removing the foregoing described contaminating influences from hydrocarbon mixtures is well known within the art of petroleum refining. Heretofore, in the field of catalytic processing, two approaches have been advanced: liquid-phase hydrogenation and vapor-phase hydrocracking. In the former type of process, the oil is generally passed upwardly while in liquid-phase and in admixture with hydrogen, through a fixed-bed or slurry of sub-divided catalyst. Although perhaps partially effective in removing nitrogenous and sulfurous compounds, this type of process is relatively ineffective with respect to the oil-insoluble asphaltics and metallic complexes. The probability of forming simultaneous contact between the asphaltene molecule and the catalytically active site is remote. Furthermore, since the hydrogenation zone is maintained at an elevated temperature of at least about 500°F. (932°C.), the retention of unconverted asphaltics, suspended in a liquid-phase oil, for an extended period of time, will result in heavy carbonaceous deposit upon the catalytic particles. The rate of diffusion of the oil-insoluble asphaltics is significantly lower than that of the other components of the hydrocarbon charge stock; for this reason, a fixed-bed catalytic process in which the oil and hydrogen are passed in a downwardly direction, is virtually precluded. The asphaltene, being neither volatile, nor dissolved, are incapable of movement to the inner catalytically active sites, these being obviously immovable, as a result of which the asphaltenes tend to agglomerate. Vapor-phase hydrocracking is carried out either with a fixed-bed, or an expanded-bed system at temperatures substantially above about 950°F. While this technique obviates to some extent the drawbacks of liquid-phase hydrogenation, it is not entirely well suited to treating metal-containing charge stocks due to the production of coke and carbonaceous material, with the result that the catalytic composite succumbs to a relatively rapid degree of deactivation.

To summarize, the metals and sulfur concentrate within the asphaltene fraction, and causes severe catalyst activity loss not recoverable by ordinary regeneration techniques. As hereinafter indicated, one embodiment of the present invention involves the removal of metals and sulfur prior to effecting conversion by way of a catalytic process. In addition to coal, or the heavy hydrocarbonaceous oil which might be extracted therefrom, the process described herein is generally applicable to those petroleum crude oils and heavy hydrocarbon fractions which are generally referred to in the art as "black oils." Exemplary of such black oil charge stocks include a "tipped" Middle-East Kuwait crude oil, having a gravity of 11.0° API, and containing 10.1% by weight of asphaltics and about 5.2% by weight of sulfur. A vacuum bottoms from a full boiling range crude oil having a gravity of 5.2° API, a Conradson carbon factor of 23.8 wt. percent, containing about 3.5% by weight of sulfur. A vacuum bottoms from a Venezuelan crude oil having a gravity of 10.2° API, a Conradson carbon factor of 13.1 wt. percent, con-
taining 3.1% by weight of sulfur, 68 p.p.m. of nickel and 460 p.p.m. of vanadium.

OBJECTS AND EMBODIMENTS

The principal object of the present invention resides in the recovery of nickel and vanadium from solid hydrocarbonaceous material such as coal and hydrocarbonaceous coke.

A corollary objective is the recovery of nickel and vanadium in the readily marketable form of the oxides thereof.

A specific object of the present invention is to provide a process for the recovery of nickel and vanadium from black oil charge stocks.

In a broad embodiment, therefore, the present invention relates to a process for recovering nickel and vanadium from hydrocarbonaceous, sulfur-containing coke, which process comprises the steps of: (a) comminuting said coke with an alkali metal halide and burning said coke to obtain a mixture of carbon dioxide, sulfur dioxide, and a fused residue containing alkali metal vanadate and nickel halide; (b) contacting said mixture with water and forming a slurry of vanadium pentoxide, sulfur dioxide and a sulfuric acid solution of nickel halide; (c) separating and recovering vanadium pentoxide from said slurry; (d) removing sulfur dioxide from said slurry and adding ammonia and carbon dioxide to the substantially sulfur dioxide-free slurry; (e) treating the substantially sulfur dioxide-free slurry to convert said nickel halide to insoluble nickel carbonate and ammonium halide, and separating said insoluble carbonate from the treated slurry effluent; and (f) calcining said separate nickel carbonate, at a temperature sufficient to decompose the same into nickel oxide and carbon dioxide, and recovering said nickel oxide.

A more limited embodiment of the present invention affords a process for recovering nickel and vanadium from a sulfur-containing, salt-contaminated hydrocarbonaceous coke stock, which process comprises the steps of: (a) desalting said charge stock and separating the desalted charge to provide a residuum fraction containing hydrocarbonaceous material boiling above a temperature of about 1050°F. and a distillable fraction consisting of hydrocarbons boiling below about 1050°F.; (b) coking said residuum fraction to provide an additional distillable fraction and hydrocarbonaceous coke containing sulfur and combined nickel and vanadium; (c) commingling salt with said coke and burning said coke to obtain a mixture of a residue containing sodium vanadate and nickel chloride, carbon dioxide, sulfur dioxide, and salt being in an amount at least 10% more than the stoichiometric quantity required to produce said chloride and vanadate; (d) scrubbing said mixture with water and forming a slurry of sulfur dioxide, vanadium pentoxide and a sulfuric acid solution of nickel chloride; (e) separating and recovering said vanadium pentoxide from said nickel chloride-containing slurry; (f) removing sulfur dioxide from said slurry and adding ammonia and carbon dioxide to the substantially sulfur dioxide-free slurry; (g) treating the substantially sulfur dioxide-free slurry to convert said nickel chloride to insoluble nickel carbonate and ammonium chloride, and separating said carbonate from the thus-treated slurry; and, (h) calcining said nickel carbonate, to decompose the same into nickel oxide and carbon dioxide and recovering said nickel oxide.

Other objects and embodiments, as hereinafter set forth in greater detail, are principally concerned with particularly preferred processing techniques and the range of various process variables. These will become evident from the following additional description of the process.

SUMMARY OF INVENTION

In summarizing the present invention, it will be presumed that the source of the nickel and vanadium is a salt-containing petroleum crude oil. It is understood, however, as hereinafter set forth, that the source of the nickel and vanadium may be a solid hydrocarbonaceous material such as coal and/or coke. The initial operation consists of desalting the petroleum crude oil. Since the desalting of petroleum crude oil is so thoroughly defined and well known in the petroleum refining art, and the operation forms no essential feature of the present invention, aside from being a possible source of salt employed in a subsequent step, a detailed description of this operation is not presented herein.

The desalted crude oil is introduced into a suitable fractionation system for the purpose of concentrating the metal-containing asphaltenes in a residuum fraction containing hydrocarbons boiling above 1050°F. Following the removal, or separation of the distillables, the residuum fraction is subjected to coking. This coking operation may be effected in the manner commonly referred to in the art as "delayed coking," and in accordance with any of the well defined coking techniques. The hydrocarbonaceous coke resulting from the coking operation, containing essentially all the metals and high molecular weight sulfur compounds is mixed with salt, preferably sodium chloride, a portion of which may be that removed from the full boiling range crude oil in the desalting operation. Although other alkali metal halides may be employed in admixture with the coke, including alkali metal iodides, fluorides, and bromides, the alkali metal chloride (especially sodium chloride) is preferred primarily from the standpoint of economics. The salt, including that resulting from the desalting operation, is admixed with the coke in a manner such that the amount of salt at least 10% more than the stoichiometric quantity required to convert the metals contained in the coke into alkali metal vanadate and nickel halide, and preferably about 50.0% more than the stoichiometric quantity.

In order to form the nickel halide and the alkali metal vanadate, the coke is burned at temperatures sufficiently high to fuse the metals and the salt. Therefore, the coke-burning temperature is controlled at a level of about 1400°F. to about 1700°F. In most present-day refinery operations, the burning of coke is perhaps best utilized in the generation of steam, utilizing sufficient excess air to minimize the quantity of carbon monoxide. The metallic salts, for example sodium vanadate and nickel chloride, as well as the carbon dioxide and sulfur dioxide, must be concentrated in some fashion if they are to be recovered as a product stream. Various techniques such as electrostatic precipitation, sulfur dioxide absorption, etc., might be used. However, a preferred method involves scrubbing the material with water.

In the water scrubber, the sulfur dioxide will dissolve to form sulfuric acid. Since both sodium vanadate and nickel chloride are soluble in the dilute acid, they are readily removed from the stream of gas resulting from the burning of the coke. The effluent from the water scrubber is transferred to a suitable settling drum, in admixture with sulfuric acid. Sulfuric acid is added in an amount sufficient to maintain a pH less than 3.0 in the settling drum. An acceptable pH range is 2.0 to 3.0. The temperature of the contents within the settling drum is maintained within the range of 150°F. to about 250°F. Under these conditions, the sodium vanadate will react within the settler to form an insoluble precipitate of vanadium pentoxide which may be withdrawn. In order to maintain acceptable water vapor-liquid content within the scrubber, liquid is recycled from the settling drum.

The vanadium pentoxide, withdrawn from the settling drum is recovered by the relatively simple expedience of filtration. Sulfur dioxide will be recovered from the resulting filtrate by stripping the same with air. The sulfur dioxide can be purified by any known technique such as adsorption, or it may be employed as the raw material in the production of sulfuric acid. Ammonia and carbon dioxide are added to the resulting sulfur dioxide filtrate, or slurry, and the mixture is subjected to conversion such that insoluble nickel carbonate is formed. Since the conversion of nickel chloride to insoluble nickel carbonate requires an alkaline environment, the quantity of the ammonia added to the sulfur
dioxide-free slurry, or filtrate, is such that the converted effluent stream contains in excess of about 2.0% by weight of ammonia. The insoluble nickel carbonate is recovered by way of a second filtration operation, and is subjected to high-temperature calcination in an atmosphere of air to convert the same into nickel oxide.

As hereinafter indicated in an example discussed in conjunction with the accompanying drawing, while the metals level in the coke appears low, there is a production of about 7.0 lb. of vanadium per hour per thousand barrels per day of residual charged to the coking operation. On the basis, the average delayed coking unit, having a capacity of about 10,000 b.p.a.d., would produce approximately 70 lbs. of vanadium and 12 lbs. of nickel each hour.

The accompanying figure will be described in conjunction with a commercially-scaled unit designed to process 25,000 bbl./day of Tigre Crude Oil. It is understood that the charge stock, steam compositions, operating conditions, vessel designs and the likes, are exemplary only, and may be varied widely without departure from the spirit of my invention, the scope of which is defined by the appended claims.

**DESCRIPTION OF DRAWING**

With reference now to the drawing, one embodiment is presented by means of a simplified flow diagram in which details such as pumps, instrumentation and controls, heat-exchange and heat-recovery circuits, valves, start-up lines and similar hardware have been eliminated as being non-essential to a clear understanding of the techniques involved. The use of such miscellaneous appurtenances, to modify the process, are well within the purview of one skilled in the art.

The Tigre Crude Oil is introduced into the processing scheme by way of line 1, being transmitted thereby into desalter 2. Crude oil desalting is an old operation, and is rather well described in the literature. Reference is made for example, to Petroleum Refinery Engineering, W. L. Nelson, McGraw-Hill, pp. 244-246 (1949), for typical desalting installations. The substantially desalted crude oil is withdrawn via line 3 into fractionator 4 wherein separation is effected to provide a distillable hydrocarbon stream in line 7 and a metal-containing residue fraction in line 8. Although indicated as a single vessel for simplification and clarity, it is understood that fractionator 4 may be an intricate system including vacuum columns, hot separators and flash zones, etc. The function of the system is to provide the feed stream to coking unit 9, being the residue fraction in line 8. As heretofore set forth with respect to the desalting operation, the delayed coking of heavy reduced crudes is an operation which is well defined in the literature, and reference is once again directed toward Petroleum Refinery Engineering, supra, pp. 603, 612-3.

The residue fraction in line 8 is about 40.0% by volume, or approximately 10,000 bbl./day, based upon the crude oil charged in line 1. An analysis of this material, the charge to coking unit 9, is presented in the following Table I:

| Gravity * API | 5.2 |
| UOP K-factor | 11.5 |
| Sulphur, wt. percent | 3.3 |
| Conradson carbon, wt. percent | 23.8 |

Metals, w.p.p.m.:
- Iron | 4.5 |
- Nickel | 92.0 |
- Vanadium | 460.0 |

The distillable hydrocarbons are indicated as leaving coker 9 by way of line 11, by which they are admixed with the virgin distillate fraction in line 7, the mixture forming a normally liquid product stream which may be further processed in accordance with one or more suitable refining techniques. On the basis of 1,000 bbl./day (15,103 lbs./hr.) charged to coker 9, the products, being the distillables in line 11 and the coke in line 12, are presented in the following Table II:

| Hydrogen Sulfide and gaseous hydrocarbons | 1,498 | 9.6 |
| Hexane | 409 F | 1,008 | 18.0 |
| 400 F, plus | 0.5 | 5.0 |
| Coke | 0.5 | 6,410 | 62.5 |

Other analyses indicate that the metals content of the two distillable fractions, pentane-400° F. and 400° F.-plus, is negligible, while the coke contains 4.6% by weight of sulfur, approximately 0.023% by weight of nickel, and about 0.107% by weight of vanadium.

The metal-containing coke, in which the nickel and vanadium most likely exist in some complex with sulfur, is intimately commingled with an alkali metal halide in line 6. In the embodiment illustrated in the accompanying drawing, since the crude oil in line 1 is initially subject to a desalting technique, at least a portion of the salt in line 6 may be supplied by way of line 5 from desalter 4. The coke and salt continue through line 6 into the refinery steam generation system 13, wherein the coke is burned in an excess of air. Although not indicated in the drawing, it will be evident that the salt and coke in line 6 should be admixed in relatively small particle size—i.e. in a ball mill, or colloid mill. The burning of the coke is effected at a temperature which results in fusion of the salt with the metals, and such temperature is preferably controlled at about 1500° F. to about 1600° F. The quantity of alkali metal halide in the instant example, sodium chloride, which is admixed with the coke, should be at least 10.0% in excess of the stoichiometric amount required to convert all the nickel and vanadium into nickel chloride and sodium vanadate. The computation of the quantity of salt necessary is based upon the assumption that the nickel and vanadium exist within the coke as NIS and V₃S₅. Upon burning, these are converted into the oxide forms of the metals, and, in the presence of sodium chloride, the conversion of the oxides to nickel chloride and sodium vanadate takes place. Preferably, the salt is admixed in an amount of from about 40.0% to about 80.0% in excess of the stoichiometric requirement. Utilization of the heat resulting from the burning of the coke will depend primarily upon the peculiar requirements of the particular refinery; in the illustrated embodiment, the heat is employed in steam generation system 13. The resulting sodium vanadate and nickel chloride, in addition to carbon dioxide and sulfur dioxide, are transferred via line 14 into scrubber 15.

While various techniques such as electrostatic precipitation, adsorption, etc., may be suitably utilized to separate and recover the nickel and vanadium salts from the carbon and sulfur oxides, countercurrent scrubbing with SO₂-saturated water is preferred from the standpoint of ease of operation and economics. Water is introduced into scrubber 15 by way of line 16 entering the scrubber in the upper portion thereof. As the scrubbing operation continues, the material in line 16 will be found to comprise SO₂-saturated water (H₂SO₄), soluble nickel chloride and soluble sodium vanadate, the various concentrations eventually attaining some steady-state level. In the scrubber, the descending stream of water counter currently contacts an ascending stream of carbon dioxide and sulfur dioxide. Additionally, sulfurous acid is formed, in which both sodium vanadate and nickel chloride are soluble. Carbon dioxide, air and minor amounts of carbon monoxide and sulfur dioxide are removed from scrubber 15 through line 17, and the sulfurous acid solution of the nickel and vanadium salts is withdrawn via line 18, being introduced thereby into settler 19. The temperature within the settler 19 is preferably controlled.
at a level of about 150°F to about 200°F. Sulfuric acid is commingled, by way of line 38, with the sulfuric acid solution in line 18 in an amount sufficient to maintain a pH less than 3.0 within the settler. Under these conditions, ammonium vanadate is formed. A recycle stream is maintained from the upper portion of the settler to the scrubber, via line 16, to provide acceptable vapor-liquid contact in scrubber 15. Additional water, as needed to maintain the balance of the system, may be introduced by way of this recycle line.

The acid solution of nickel chloride and the insoluble vanadium pentoxide is introduced to filtration system 21 through line 28. Vanadium pentoxide is withdrawn as a filter cake through line 22 and, after drying to remove the final traces of physically-held water, is recovered in an amount of about 12.2 lbs./hr. of which 6.8 lbs./hr. represents vanadium metal. The nickel chloride-containing filtrate is transferred by way of line 23 into the upper portion of stripper 24 wherein it contacts an ascending stream of air to effectively strip sulfur dioxide, the latter being removed by way of line 25. The stripping medium, air, is introduced into the stripping column of stripper 24 through line 26. The SO₂-free filtrate is removed by way of line 27, and is admixed with ammonia being introduced by way of line 28, the mixture containing there through into converter 29. The converter is maintained at temperature and pressure conditions selected to convert the soluble nickel chloride into insoluble nickel carbonate, carbon dioxide also being introduced through line 30. Suitable pressures range from 200 psig to about 500 psig, while moderate temperatures are from 250°F to about 350°F. Sufficient ammonia is added to provide at least 2.0% by weight free ammonia in the converter effluent stream in line 31. This insures a basic environment in converter 29, thus enabling the conversion of the soluble nickel chloride to insoluble nickel carbonate. The converter effluent is passed through line 31 into filtration system 32 wherein a filtrate of ammonium chloride is removed through line 33. The insoluble nickel carbonate, as a filter cake, is introduced into calciner 35 by way of line 34, wherein it is calcined in an atmosphere of air at a temperature sufficiently high to decompose the same into nickel oxide and carbon dioxide. A temperature of about 1000°F, or higher, for a period of about two hours, or longer, is sufficient. The carbon dioxide is removed from line 33, and may be introduced into converter 29, via line 30, to form therein additional nickel carbonate. Nickel oxide, in an amount of 1.67 lbs./hr., is removed via line 37; this quantity of nickel oxide represents 1.31 lbs./hr. of elemental nickel.

On the original basis of 10,000 bbl./day of atmospheric bottoms charged to the coking unit 9, about 68.0 lbs./hr. of vanadium and 13.1 lbs./hr. of nickel are recovered. Considering only the vanadium, the daily quantity is approximately 1,632 pounds, or 506,000 lbs./year on the basis of 310 operating days. This figure attains greater significance when it is realized that it represents approximately 4.6% of the current domestic vanadium production of about eleven million pounds per year.

The foregoing specification illustrates the metal recovery process encompassed by the present invention and indicates the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for recovering nickel and vanadium from hydrocarbonaceous, sulfur-containing coke, which process comprises the steps of:
(a) commingling said coke with an alkali metal halide in an amount at least 10% in excess of the stoichiometric amount required to convert nickel and vanadium into nickel halide and alkali metal vanadate and burning said coke at a temperature sufficient to form alkali metal vanadate and nickel halide and to obtain a mixture thereof with carbon dioxide and sulfur dioxide;
(b) contacting said mixture with water to form a sulfuric acid solution of nickel halide and alkali metal vanadate and separating carbon dioxide from said solution;
(c) maintaining the temperature of said solution within the range of 150°F to about 250°F and adding acid in an amount sufficient to maintain a pH of less than 3.0 to form insoluble vanadium pentoxide and separating said vanadium pentoxide from said solution;
(d) removing sulfur dioxide from said solution by stripping with air and adding ammonia and carbon dioxide to the substantially SO₂-free solution;
(e) subjecting the SO₂-free solution to conditions of temperature and pressure sufficient to convert said nickel halide to insoluble nickel carbonate and ammonium halide, and separating said insoluble carbonate from the treated solution; and,
(f) calcining said separated nickel carbonate, at a temperature sufficient to decompose the same into nickel oxide and carbon dioxide, and recovering said nickel oxide.

2. The process of claim 1 further characterized in that sufficient ammonia is added to said substantially SO₂-free solution to provide at least 2.0% by weight of ammonia in the resulting treated solution.

3. The process of claim 1 further characterized in that said alkali metal halide is sodium chloride.

4. The process of claim 1 further characterized in that at least a portion of the carbon dioxide resulting from the decomposition of said nickel carbonate is admixed with said substantially SO₂-free solution.

5. A process for recovering nickel and vanadium from a salt-containing, sulfur-contaminated hydrocarbon charge stock, which process comprises the steps of:
(a) desalting said charge stock and separating the desalted charge to provide a residue fraction containing hydrocarbonaceous material boiling above a temperature of about 1050°F and a distillable fraction consisting of hydrocarbons boiling below about 1050°F;
(b) coking said residuum fraction to provide an additional distillable fraction and hydrocarbonaceous coke containing sulfur and combined nickel and vanadium;
(c) commingling sodium chloride with said coke and burning said coke at a temperature sufficient to provide a mixture of a residue containing sodium vanadate and nickel chloride, carbon dioxide and sulfur dioxide, said sodium chloride being in an amount at least 10% more than the stoichiometric quantity required to produce said chloride and vanadate;
(d) scrubbing said mixture with water to form a sulfurious acid solution of nickel chloride and sodium vanadate and separating carbon dioxide from said solution;
(e) maintaining the temperature of said solution within the range of 150°F to about 250°F and adding acid in an amount sufficient to maintain a pH of less than 3.0 to form insoluble vanadium pentoxide and separating said vanadium pentoxide from said nickel chloride-containing solution;
(f) removing sulfur dioxide from said solution by stripping with air and adding ammonia and carbon dioxide to the substantially SO₂-free solution;
(g) subjecting the SO₂-free solution to conditions of temperature and pressure sufficient to convert said nickel chloride to insoluble nickel carbonate and ammonium chloride, and separating said carbonate from the treated solution; and,
(h) calcining said nickel carbonate, to decompose the same into nickel oxide and carbon dioxide, and recovering said nickel oxide.
6. The process of claim 5 further characterized in that at least a portion of the salt added to said coke is supplied by the desalting of said charge stock.

7. The process of claim 6 further characterized in that at least a portion of the carbon dioxide resulting from the decomposition of said nickel carbonate is admixed with said substantially SO₂-free solution.

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