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R. J. FIOCCO ET AL

3,790,467

COAL LIQUEFACTION SOLIDS REMOVAL

Filed April 24, 1972

3 Sheets-Sheet 1

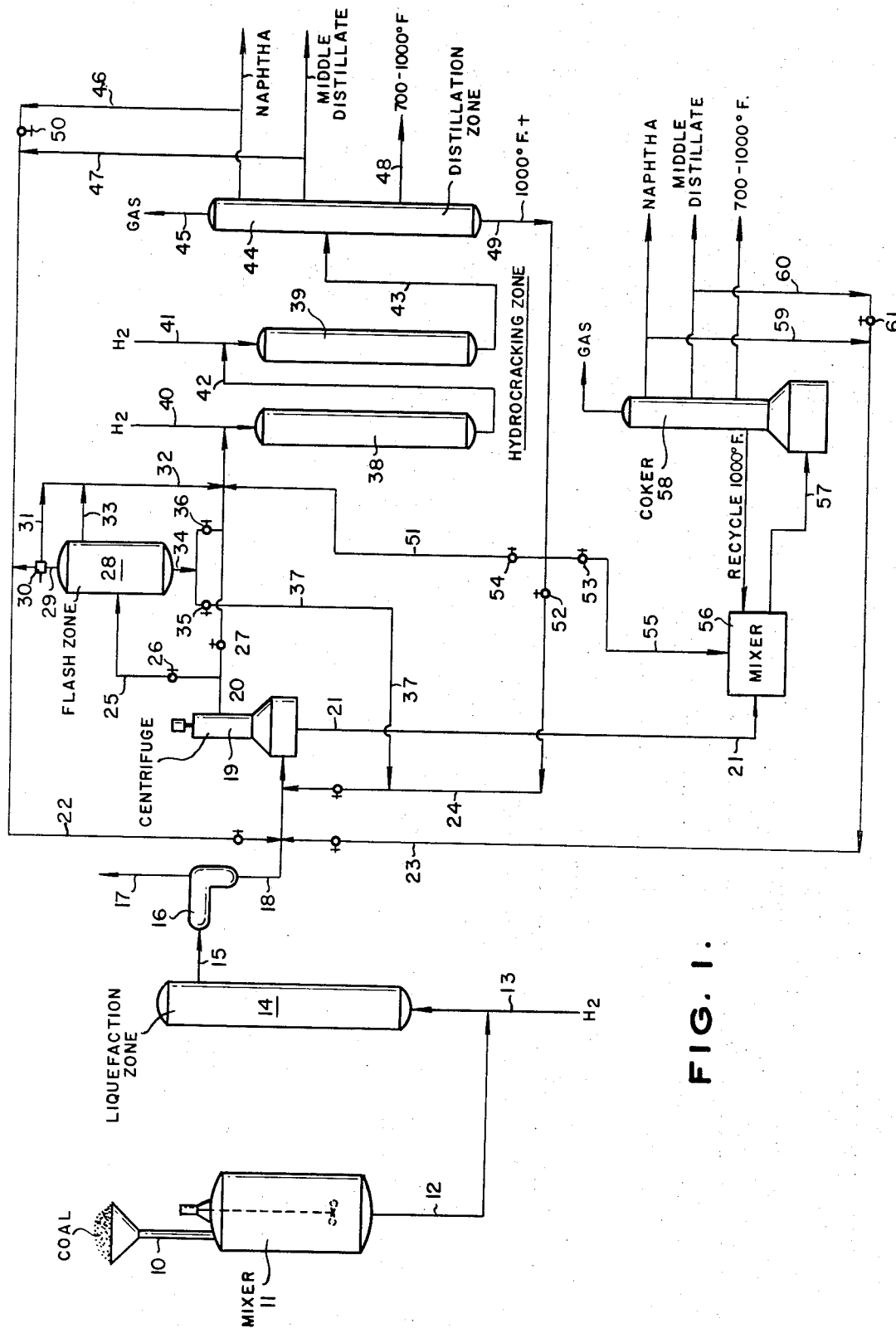


FIG. 1.

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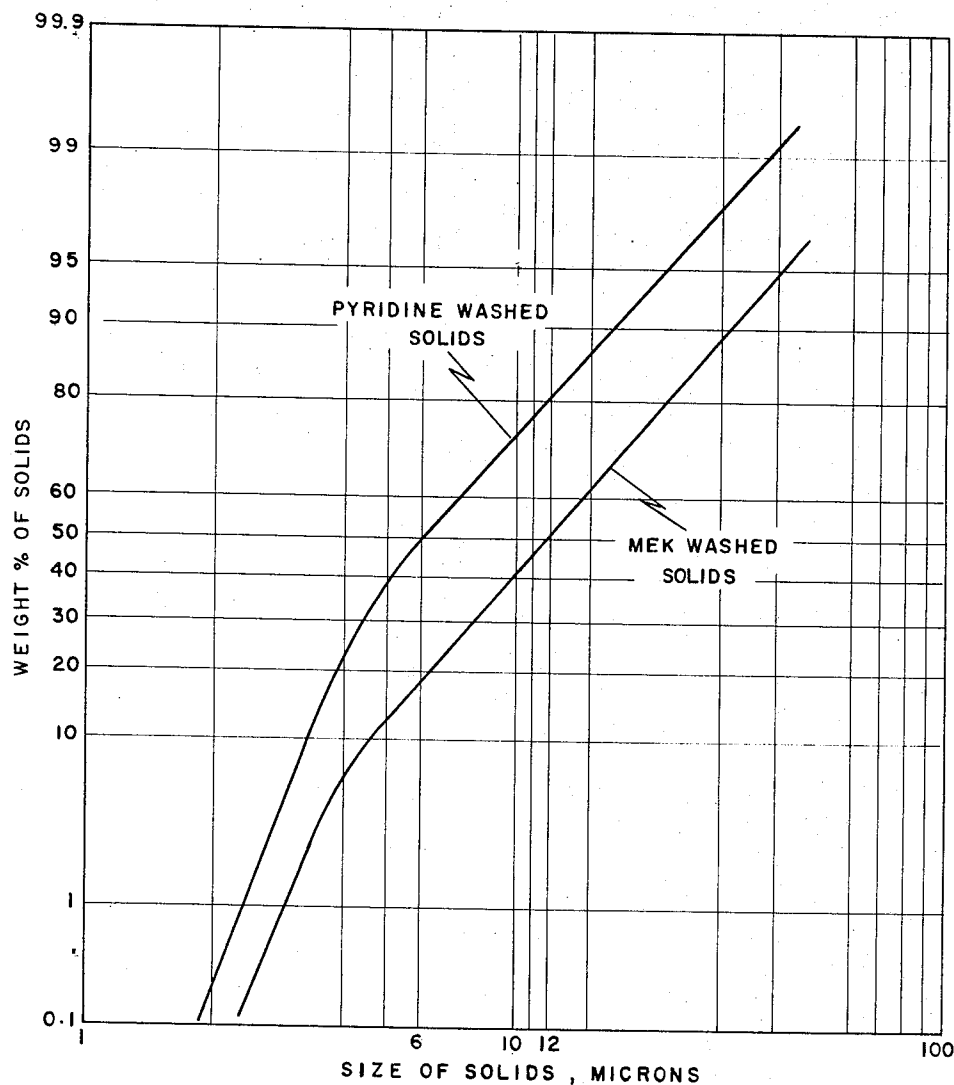


FIG. 2.

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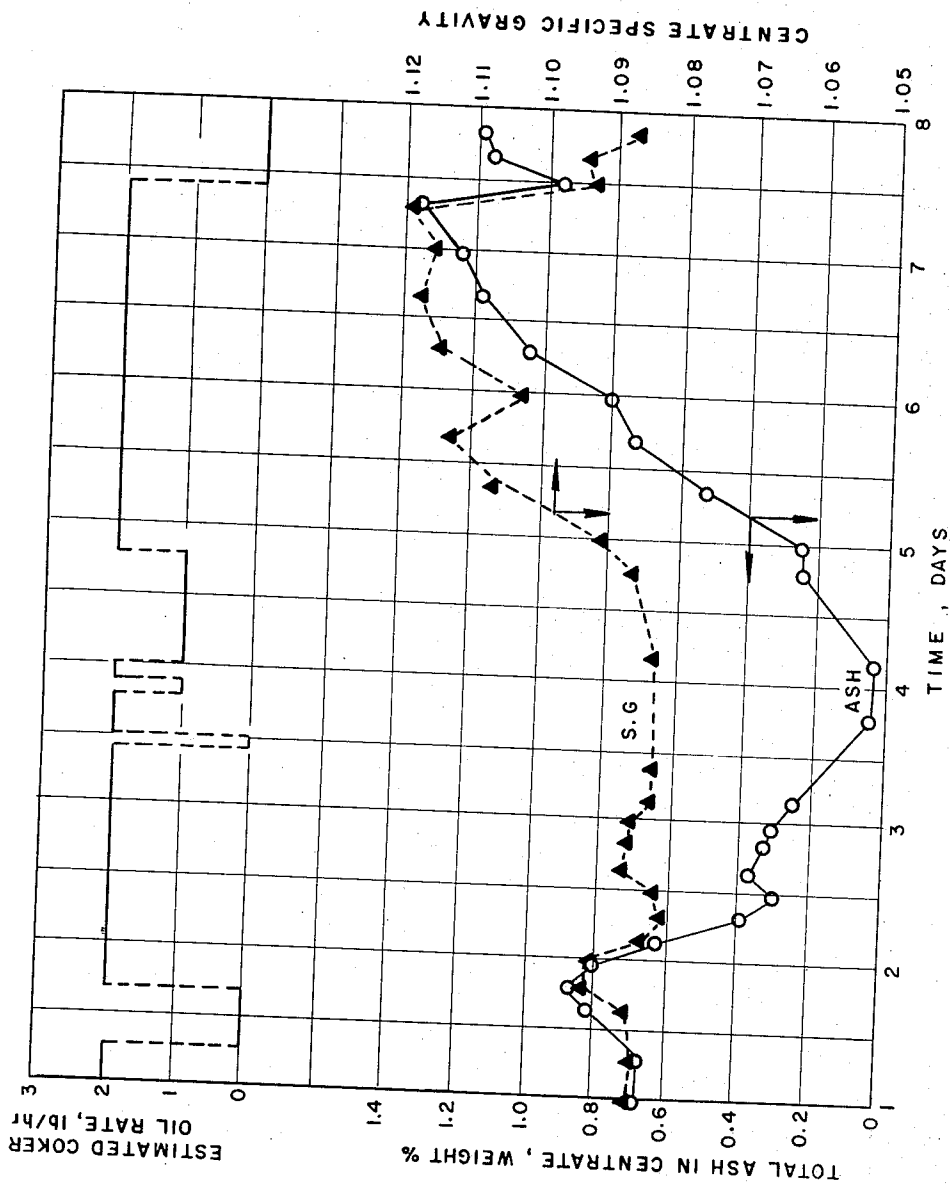


FIG. 3.

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COAL LIQUEFACTION SOLIDS REMOVAL

Robert J. Fiocco, Summit, N.J., and Edward L. Wilson, Baytown, Tex., assignors to Esso Research and Engineering Company

Continuation-in-part of application Ser. No. 67,457, Aug. 27, 1970, now Patent No. 3,687,837. This application Apr. 24, 1972, Ser. No. 246,725

The portion of the term of the patent subsequent to Jan. 29, 1989, has been disclaimed

Int. Cl. C10g 1/04

U.S. Cl. 208—8

12 Claims

ABSTRACT OF THE DISCLOSURE

Solid residues are more effectively separated from a coal extract enriched solvent of a coal liquefaction product, in a solids-liquids separation zone in which solids size is a separation parameter, by adding to the coal liquefaction product a coal extract liquid derived from the coal liquefaction product and containing at least 20 volume percent of materials boiling below about 400° F. or at least 20 volume percent of materials boiling above about 1000° F.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 67,457, filed Aug. 27, 1970 and entitled "Coal Liquefaction Solids Removal," now U.S. Pat. 3,687,837.

BACKGROUND OF THE INVENTION

This invention relates to the production of liquid fuels from solid coal, and more particularly, to a step in such processes in which undissolved solids in a coal extract enriched solvent of a coal liquefaction product are separated from the enriched solvent according to the size of the solids.

In the upgrading of coal by hydrogen transfer and cracking to obtain liquid fuels such as gasoline and kerosene, a number of processes are carried out to transfer hydrogen to the basic coal molecules, to break up the coal molecules into smaller fragments, and to remove sulfur and nitrogen from the products. The basic coal liquefaction step may be carried out in a number of ways, but it is preferred to use a hydrogen-donor solvent, such as hydrogenated creosote oil or an indigenous hydrogenated product boiling in a middle distillate range which is obtained in the liquefaction of coal. Extraneous molecular hydrogen may be added to the liquefaction zone, if desired. All of this, directed to the basic liquefaction of coal, is old in the art, as disclosed in various patents such as U.S. Pats. 3,018,241 and 3,117,921.

The product of coal liquefaction is a mixture of liquefied coal extract (some of which has been cracked and hydrogenated), solvent, and undissolved solids, including unconverted organic solids and ash solids. The solids are conventionally separated from the liquefied extract and solvent by centrifugation, filtration, or other solids-liquid separation processes in which solids are separated from liquids according to the size of the solids. Thereafter the clarified extract enriched solvent is upgraded by various processes, typically including catalytic hydrocracking, in order to produce liquid fuel products.

In processes in which the clarified extract enriched sol-

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vent from the solids-liquid separation zone is passed into a catalytic hydrocracker for upgrading, extremely small solids (for example, 10 microns and less) remaining in the clarified liquid can block catalyst pores and eventually produce channeling in the bed. It is important that these extremely small particles be removed from the liquid extract before hydrocracking of the extract.

Heretofore, in U.S. Pat. 3,018,241, it was suggested that benzene insoluble solids can be separated from the extract enriched solvent by the addition of a low-boiling paraffinic antisolvent, specifically hexane. On a commercial scale, however, the suggestion is impractical. Addition of such antisolvents precipitates considerable amounts of the benzene soluble coal extract liquid gained by coal liquefaction, decreasing the yields of liquid extract to the extent that, as a method of improving solids removal from the coal liquefaction product, use of such antisolvents is economically prohibitive. It is therefore highly desirable and plainly important that more economical and more usefully effective measures be discovered for improving the removal of solids from coal extracts produced in coal liquefaction processes. This invention is directed to that end.

SUMMARY OF THE INVENTION

This invention provides a new method for improving the removal of solids, particularly very small solids on the order of 10 microns and less, from the coal extract enriched solvent of a coal liquefaction product, while preserving the yields of coal extract obtained in a coal liquefaction process.

According to the invention, a coal extract liquid derived from the coal liquefaction product and containing at least about 20 volume percent of materials boiling below about 400° F. or at least about 20 volume percent of materials boiling above about 1000° F. is added to the coal liquefaction product in an amount which is effective to make at least a portion of the smaller and difficultly separable solids in the coal liquefaction product into solids that are larger and more easily separable in a solids-liquids separation zone wherein solids size is a separation parameter.

Coal derived materials boiling below about 400° F. or above about 1000° F. are so sufficiently dissimilar to the coal extract enriched solvent that they are able to cast from solution or resolidify small amounts of "quasi-solid" coal extract materials liquefied in a deep extraction of the coal; however, the coal derived materials boiling below about 400° F. or above about 1000° F. are not so dissimilar from the extract enriched solvent that they noticeably cause other liquefied coal extract materials to be cast from solution. It has been found that the small amounts of "quasi-solid" materials so cast from solution are effective to cause a sufficient increase in size of smaller, difficultly separable solids that such solids are made more separable from the extract enriched solvent in a solids-liquids separation zone such as a centrifuge, filter, cyclone or other type of such zone in which solids size is a parameter of separation. Because only small amounts, typically less than about 5 weight percent of the "quasi-solid" materials are cast from solution, and also because substantially no other coal extract materials than the "quasi-solids" are so cast from solution, the yield of coal extract materials obtained by the coal liquefaction operation is preserved.

The coal derived liquid which is added to the coal liquefaction product to improve solids removal in a solids-liquids separation zone preferably is obtained from the clarified extract enriched solvent, before or after a hydrocracking operation conducted on such solid, or in the case of a coal extract liquid derived from the coal liquefaction product and containing about 20 volume percent of materials boiling below about 400° F., from a fraction of a coker oil stream produced by coking the slurry of solid residues obtained from the solid-liquid separating zone.

In general, whichever fraction is used, suitable increases in coal extract clarity can be obtained by adding the fraction of coal derived liquid to the liquefaction product in amounts of from about 1 to about 50 weight percent of the resulting feed to the separation zone.

As an aspect, it has been found that a desired clarity of the coal extract issuing from the separation zone in a continuous process can be maintained by adding to the liquefaction product more or less of a fraction of a coal derived liquid which contains at least 20 volume percent of materials boiling below about 400° F., as needed to keep the specific gravity of the clarified extract below a predetermined value in the range from about 1.08 to about 1.12 above which a desired level of clarity is not obtained.

Other aspects and advantages of the invention will be more evident from a description of preferred methods of carrying out the invention, taken in conjunction with the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram of preferred modes of carrying out the invention;

FIG. 2 is a plot of the weight percent of solids smaller than a given size versus the particle sizes of pyridine-washed solids and methyl ethyl ketone-washed solids of a liquefaction product prepared as described in Example 1, where the plot is discussed; and

FIG. 3 is a plot of the ash content and specific gravity of the overflow concentrate from a centrifuge operated in accordance with this invention over a 140-hour period, indicating the rate of addition of a recycle coker oil fraction derived from the centrifuge underflow. FIG. 3 is discussed in Example 2.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the FIG. 1, raw coal is fed by way of line 10 into a mixer 11 which also receives by line 10 a hydrogen donor solvent, preferably an indigenous hydrogenated product boiling in a middle distillate range, suitably recycled from line 47. The coal is slurried in the solvent oil, and the slurry is withdrawn by way of line 12. Any suitable coal-like material may be used as a feedstock, for example, subbituminous coal, bituminous coal, lignite or brown coal. The coal is generally ground to a particle size of about -8 mesh (Tyler screen) and finer and may be dried before it is fed into the mixer 11. The solvent/coal weight ratio is suitably within the range from about 0.8 to about 10, and preferably from about 1 to about 2.

The slurry may be mixed with hydrogen introduced by way of line 13 and then passed into a liquefaction reactor 14. Within the liquefaction reactor, the coal is allowed to dissolve under conditions of high temperature and pressure, such as a temperature within the range from about 650° F. to about 900° F. and a pressure from about 350 p.s.i.g. to about 2500 p.s.i.g. The hydrogen-treat rate (if hydrogen is used) may be fairly low, and may suitably range from about 100 to about 1000 s.c.f./b. of coal slurry charge. In the liquefaction reactor, the coal is depolymerized and partially thermally cracked, and a liquefaction product is withdrawn, by way of line 15, which

comprises the liquefied coal extract, at least a partially depleted hydrogen-donor solvent, and undissolved solids, including ash solids. The hydrogen and noncondensable gases are separated from the liquid and solid components in a separator 16 and are removed by way of line 17, while the slurry is carried by line 18 to a separation zone 19 which separates solids from liquids according to sizes, separately issuing a clarified coal extract and a concentrated solid slurry. Separation zone 19 is suitably a filter, a hydrocyclone, or, as illustrated, a centrifuge, in which case the clarified coal extract issues as a concentrate overflow 20 and the concentrated solids slurry issues as an underflow 21.

In accordance with this invention, there is added to the coal liquefaction product feeding to centrifuge 19, a fraction of a coal extract liquid containing at least about 20 volume percent of materials boiling below 400° F. or above 1000° F., suitably a clarified coal extract fraction boiling within the range of from about 100° F. to about 700° F. or above 1000° F. and containing ash solids, or a distillate fraction of boiling in the range of from 100° F. to 700° F. obtained from products derived from coking the concentrated solids slurry from separation zone 19.

The added fraction of clarified coal extract having 20 volume percent of material boiling below 400° F. may be obtained from the clarified coal extract without subjecting the extract to further treatment after it issues from the separation zone. Thus, the clarified coal extract may be fractionated, as in a pressure reduction flash zone fractionation hereinafter described, to recover such fraction which then is recycled for addition to the liquefaction product. Alternatively, the clarified coal extract may be further treated to upgrade the extract. For example, the clarified coal extract may be hydrotreated to saturate the unsaturated mono and polynuclear rings of the extract to a desired level; or in a more severe treatment, the clarified coal extract may be hydrocracked to convert high-boiling aromatic compounds to lower boiling and saturated compounds of naphthenic character. The use of a hydrocracking process is hereinafter described to illustrate this aspect of the invention. The desired fraction can be recovered from the hydrotreated or hydrocracked effluent and recycled for addition to the feed to the centrifuge.

In the drawing, reference numeral 22 indicates a recycle line of clarified coal extract boiling within the range of from about 100° F. to about 700° F. and containing at least about 20 volume percent of materials boiling below about 400° F.; reference numeral 23 indicates a recycle line of coker oil distillate fractions boiling within the 100° F. to 700° F. range, having at least 20 volume percent of materials boiling below about 400° F. and recovered from the coked concentrated solids slurry underflow from centrifuge 19; and reference numeral 24 indicates a recycle line of a clarified coal extract fraction boiling above about 1000° F. and containing ash solids.

Whichever of the fractions from lines 22, 23, and 24 is used, sufficient of the fraction is added to produce an increase in clarification of the clarified overflow concentrate issued from the centrifuge by line 20. Suitably, the fraction added by line 22, line 23, or line 24 is in amounts of from about 1 to about 50 weight percent, preferably from about 3 to about 30 weight percent of the resulting feed to the centrifuge. Additions of more than about 50 weight percent of a recycle fraction are impractical from a cost standpoint.

When the recycle fractions boiling within the 100° F. to 700° F. range are added, the specific gravity of the clarified extract is suitably monitored. A rise in specific gravity above a predetermined level in the range of about 1.08 to 1.12 corresponding to a desired concentrate clarity is followed by addition of more of the recycle fraction, as needed, to reduce the specific gravity of the concentrate to the predetermined level.

The clarified centrate overflow from centrifuge 19, as stated above, may be fractionated without further treatment, or it may be subjected to further upgrading and then fractionated. Accordingly, in the former instance, the overflow centrate from centrifuge 19 is carried by line 25 from line 20 with the opening of valve 26 and the closure of valve 27 into a pressure reduction flash zone 28, which is operated in accordance with known technology to recover a fraction of the centrate overflow which boils within the range of from about 100° F. to about 700° F. and containing at least about 20 volume percent of materials boiling below about 400° F. The particular fraction selected within that range is discharged from the flash zone by way of line 29 and passes through a metering valve 30 which admits only as much of that fraction to recycle line 22 as is desired, the remaining portion of that fraction being diverted into line 31 for recycle to line 20 by way of line 32. Fractions of the centrate fed to the flash zone which are not wished to be recycled, i.e., fractions boiling above about 700° F. but below about 1000° F., or in a particular instance, a heavier fraction within the 100° F. to 700° F. boiling range aforesaid, are discharged from flash zone 28 by line 33 for return to line 20 by line 32.

Flash zone 28 may be operated to separate the foregoing fractions from the fraction of the overflow centrate boiling above about 1000° F., which is illustrated as discharged from flash zone 28 by way of line 34, which, when valve 35 is opened and valve 36 is closed, passes the bottoms fraction of the centrate by way of line 37 into the centrate bottoms recycle line 24. When valve 35 is closed and valve 36 is opened, line 34 returns the centrate bottoms to line 20 for upgrading.

Line 20 carries clarified centrate overflow into a hydrocracking zone, suitably comprising two reactors 38 and 39, for upgrading. The clarified centrate in line 20 may comprise all of the centrate overflow from centrifuge 19 in the instance when valve 26 is closed and valve 27 is opened, or various fractions of the centrate overflow return to line 20 by lines 36 and/or 32 when valve 27 is closed and valve 26 is opened.

In the hydrocracking zone, the clarified extract is contacted with hydrogen introduced by way of lines 40 and 41 and is passed sequentially by way of line 42 in downflow across stationary beds of catalyst granules in the reactor, suitably cobalt molybdate, nickel molybdate, nickel tungsten and palladium on various substrates, such as kieselguhr, alumina, silica, faujasites, etc. The cobalt molybdate catalyst is preferred, and may have 3.4 weight percent cobalt oxide, 12.8 weight percent molybdenum oxide, and 8.3 weight percent alumina. The catalyst may range from 2 to 5 weight percent cobalt oxide and from 10 to 15 weight percent molybdenum oxide, all as well known in hydrocracking arts.

The clarified extract passed in downflow across the catalyst beds is preferably in the liquid phase, but may be in the mixed liquid and vapor phase, hydrogen in the reactor being present in both the gas phase and dissolved in the liquid phase. Preferably, the hydrocracking reaction carried out in the reactors 23 and 24 occurs under hydrocracking conditions which include a temperature from about 650° F. to about 900° F. preferably about 750° F., a pressure of 1000 to 4000 p.s.i.g., preferably 2000 p.s.i.g., a residence time within the reactor of 30 to 300 minutes, preferably 60 minutes, and a hydrogen rate from about 3000 to about 8000 s.c.f./b., preferably about 5000 s.c.f./b., based on the total volume of liquid charged to the hydrocracking reactors.

The products of the hydrocracking reactor are removed by way of line 43 and introduced into a fractionating tower 44, where the clarified hydrocracked products are fractionated into a plurality of various fuel products streams, including: gas taken overhead by way of line 45; a stream boiling within the naphtha boiling range, from about 75° F. to 100° F. up to about 400° F., a por-

tion of which is removed by way of line 46 for recycle by way of line 22; a middle distillates stream boiling over the range from about 400° F. to about 700° F., a fraction of which may be removed by way of line 47 for introduction to recycle line 22; a heavy distillates stream boiling above about 700° F. and up to about 1000° F., which is removed by way of line 48 for use as desired; and a clarified centrate fraction boiling above about 1000° F. and containing ash solids, which is removed from distillation tower 44 by way of line 49 for recycle to line 24.

The fraction taken from the distillation tower 44 by way of line 47 may be introduced alone into line 22, or blended so as to have at least about 20 volume percent of materials boiling below about 400° F., by the closure or metering operation of a suitable valve 50.

The bottoms fraction boiling above about 1000° F. taken from distillation tower 44 by line 49 is recycled to line 20 for cracking by way of line 51 when valves 52 and 53 are closed and valve 54 is opened. The centrate bottoms fraction is recycled to line 24 for addition to the centrifuge feed by line 49 on closure of valves 53 and 54 and the opening of valve 52. When valves 54 and 52 are closed and valve 53 is opened, the bottoms fraction of the centrate is carried by way of line 55 to a mixing zone 56 where it is mixed with the underflow carried by line 21 in the mixing zone 56. Line 55 may be closed by valve 53 to prevent mixing of the underflow from line 21 and the bottoms fraction from distillation tower 44, if desired.

From mixing zone 56, effluent discharges by way of line 57 for introduction into coker 58, which preferably is operated to maintain a dense phase fluidized bed of coke particles in the lower portion thereof. Within coker 58, the liquid hydrocarbons in the underflow undergo thermal cracking, and vaporous hydrocarbon products are passed upwardly into a distillation tower suitably mounted above the coker vessel as schematically illustrated. The fractionator is operated to produce gas, naphtha, middle distillates and heavy distillates streams, as in the case of distillation tower 44, the desired fractions within the naphtha and middle distillates streams being removed to recycle line 23 by way of lines 59 and 60 respectively. The use of single portions of such fractions or blends thereof so as to recycle a stream having at least 20 volume percent of materials boiling below about 400° F. is controlled by a valve 61, as in the case of valve 50 for the fractions produced from distillation tower 44. The molecules in the fraction recycled from the coker will be more aromatic with less hydrogen content, than the molecules in the fraction recovered from tower 44, and more materials boiling below 400° F. will in general be necessary to produce a desired improvement in the clarity of the centrifuge overflow.

Although not illustrated, the vaporous product from coker 58 may be routed directly to distillation tower 44 and recovered therefrom so that the fraction recycled by line 22 is a blend of centrate overflow and underflow products.

The following table (Table I) sets out representative distillations of a coker oil product, hydrocracked naphtha and hydrocracked middle distillate products, and a centrifuge centrate produced by the embodiment of the foregoing process in which a coker oil fraction boiling within a range of from about 100° F. to about 700° F. and containing at least about 20 volume percent of materials boiling below about 400° F. was recycled to the centrifuge feed. In the embodiment, the coal liquefaction product feed rate to the centrifuge was 74 pounds per hour and the coker oil recycle feed rate to the centrifuge was 14.7 pounds per hour (16.6 weight percent of the total feed to the centrifuge). Ash content in the feed to the centrifuge was 3.2 weight percent. Centrifuge overflow liquid was recovered at the rate of 65 pounds per hour and centrifuge overflow condensate was obtained at the

rate of 1 pound per hour. Ash content of the centrifuge overflow liquid was 0.02 weight percent.

runs, the feed to the centrifuge was modified by inclusion of 10 weight percent (Run 2) and 20 weight percent (Run

TABLE I

Volume percent	Hydrocracked centrate			Centrifuge centrate	
	Coker oil temp., ° F.	Naphtha temp., ° F.	Middle oil temp., ° F.	Overflow temp., ° F.	Condensate temp., ° F.
1BP-----	286	162	335	360	-----
10-----	357	205	381	428	-----
20-----	400	214	411	460	335
30-----	435	222	433	488	355
40-----	445	230	450	525	374
50-----	468	239	486	579	389
60-----	509	250	522	633	404
70-----	572	264	565	704	419
80-----	635	279	604	815	433
90-----	724	296	675	-----	457

As seen from Table I, the coker oil stream, the hydrocracked naphtha and middle distillate streams, and the centrifuge overflow, including condensate, all contain materials boiling below 400° F. The coker oil stream is suitable for recycle as constituted. The hydrocracked naphtha

naphtha distillation range, and produced as described 3) of a hydrocracked centrate fraction boiling in the above in connection with FIG. 1. Solids in the feeds and ash solids in the centrates of Runs 1-3 were measured. The results of these runs are set out below in Table II.

TABLE II.—ADDITION OF HYDROCRACKED CENTRATE FRACTION (HCF) TO LIQUEFACTION PRODUCT (L.P.)

	Run number		
	1	2	3
Feedstock-----	L.P.	L.P.+10% HCF	L.P.+20% HCF
Feed:			
Rate, lb./min-----	30.7	27.0	27.1
Benzene insolubles, wt. percent ¹ -----	20.94	21.23	20.95
MEK insolubles, wt. percent-----	6.14	6.83	7.65
Ash, wt. percent-----	3.28	3.34	3.49
Organic MEK insolubles, wt. percent ² -----	2.86	3.49	4.16
Quasi-solids, wt. percent ³ -----	14.8	14.4	13.3
Overflow/underflow splits:			
Quasi-solids-----	2.97	4.58	3.24
Benzene solubles-----	3.02	3.88	3.24
Centrate:			
Rate, lb./min-----	21.8	20.0	19.6
Specific gravity-----	1.0901	1.0652	1.0540
Viscosity at 400° F., cp-----	3.7	3.0	2.9
Ash in centrate, wt. percent ¹ -----	0.41	0.16	0.10
Ash removed from centrate, percent-----	87.6	94.7	96.6
Ash balance, percent-----	103	101	92
Improvement in clarity, percent-----		61	75.5

¹ Weight percents are based on L.P. in feed.

² Organic MEK insolubles are MEK insolubles less ash.

³ Quasi-solids are benzene insolubles less MEK insolubles.

fraction may be recycled in whole or blended with the middle distillates fraction to adjust the middle distillate fraction so that more materials boiling below 400° F. are included in it. The middle distillate contains about 20 volume percent of materials boiling below about 400° F. and is suitable for recycle. The condensate fraction of the centrifuge overflow may be recycled in whole or blended with the liquid centrifuge overflow, as described, to produce fractions having at least about 20 volume percent boiling below 400° F. (Recycling to condensate will cause it to accumulate and build up to a higher rate than occurred in the coker oil recycle embodiment just described.)

The following examples will further illustrate the invention. In the examples, increase in liquid extract clarity is quantified by the decrease in ash content of solids in the clarified extract. In this regard, ash content of solids, or reference elsewhere herein to "ash solids," is not the same as the total mineral matter content of the solids, which also contain sulfur and carbonates, for example.

Example 1

Using a disc-nozzle type centrifuge operating at 400° F., solids (including ash solids) were separated, in three runs, from samples of the liquid extract of a coal liquefaction product resulting from heating a slurry of two parts hydrogenated creosote oil and one part -100 mesh Illinois #6 coal at 730° F. under 350 p.s.i.g. for about 45 minutes. In the first run, the liquefaction product feed to the centrifuge was unmodified. In the second and third

As may be seen by reference to Table I, in Run 1, the ash content of the centrifuge feed was reduced from 3.28 to 0.41 percent in the centrate, a reduction of 87.6 percent of the ash in the feed. Run 2, in which 10 weight percent of hydrogenated centrate fraction was added to the feed, ash content was reduced from 3.34 weight percent to 0.16 weight percent in the centrate, an improvement in centrate clarity of 61 percent over that obtained in Run 1. In Run 3, in which 20 weight percent of hydrogenated centrate fraction was added to the centrifuge feed, ash content was reduced from 3.49 weight percent in the feed to 0.10 weight percent in the centrate, an improvement in centrate clarity of 75.5 percent over Run 1.

The content of solids in the feed to the centrifuge was determined by using benzene and methyl ethyl ketone (MEK), at room temperature, as solvents to dilute samples of the liquefaction product, at least in equal volumes, and to wash the solids which separated in a laboratory analytical centrifuge. The washed solids were pyrolyzed to determine ash contents. As set forth in Table I, the benzene insoluble solids comprised solids soluble and insoluble in MEK. The solids which were insoluble in MEK had both ash constituents and organic constituents.

The following experiment was undertaken to ascertain the nature of the organic constituents.

A slurry of two parts by weight of hydrogenated creosote oil to one part by weight of -100 mesh Illinois #6 coal was liquefied at 730° F. and 350 p.s.i.g. for about 45 minutes. The liquefaction product was diluted with an equal volume of methyl ethyl ketone, the solids in the diluted liquefaction product were separated in a labora-

tory analytical centrifuge, and the solids recovered from the centrifuge were washed with MEK at room temperature. Pyridine was then used as a solvent to dilute samples of the MEK washed solids and to wash the solids which separated by filtration through Whatman No. 42 fine filter paper. Coulter counter measurements were made on samples of the MEK washed solids and on samples of the pyridine-washed solids. Solids distribution curves of the weight percent of solids less than a given size were plotted against particle sizes for the pyridine-washed solids and for the MEK washed solids. These curves are illustrated in FIG. 2.

The curves in FIG. 2 show that 50 weight percent of the pyridine-washed solids were less than 6 microns in diameter and 50 weight percent of the MEK washed solids were less than 12 microns in diameter. The pyridine-washed solids appear to closely approximate the "true" solids content of the solids in the liquefaction extract, i.e., the pyridine-washed solids are composed of the mineral matter and unconvertible organics in the liquefaction extract. The MEK washed solids, which are larger, are apparently composed of the "true" solids plus solid substances which had been dissolved in the liquid extract but which had solidified on addition of the MEK to the liquefaction extract to agglomerate the "true" solids into the larger particles. Thus, the organic constituents in the MEK insolubles in Run 1 apparently contain a slight amount of converted organic material.

Because identical solvent separation techniques were used in Runs 1-3, valid comparisons can be made between Run 1 and Runs 2 and 3.

Referring to Table II, the solids which were insoluble in benzene but soluble in methyl ethyl ketone are termed "quasi-solids." Benzene solubles are, of course, liquids. The distribution in the centrifuge of the density of benzene solubles is given by the ratio of benzene solubles appearing in the overflow to those appearing in the under flow. As Runs 1 and 3 indicate, the ratio of quasi-solids in the centrate to quasi-solids, in the under flow is essentially the same as the over flow/underflow ratio for benzene solubles. Hence, the quasi-solids can be taken to be dissolved in the liquid extract solvent at the 400° F. temperature. (Run 2 had poorer material balances of benzene and MEK insolubles, not shown in Table II, and is not illustrative in this regard.)

As Runs 1 and 3 of Table II further show, on addition of the hydrocracked centrate fraction to the coal liquefaction product feed to the centrifuge the percent of organic MEK insoluble solids in the feed increased about 1.3 weight percent, the weight percent of quasi-solids in the feed decreased by about the same amount that the organic MEK insolubles increased, and the percent of ash stayed fairly consistent. This suggests that the addition of the hydrocracked centrate fraction to the liquefaction product was instrumental in resolidifying slightly more than 1 weight percent of the liquid quasi-solids into organic MEK insoluble solids. Taken with the fact that the clarity of the centrate recovered from the centrifuge increased 75.5 percent on addition of the hydrocracked centrate fraction, the evidence suggests that the resolidification of the quasi-solids was instrumental in increasing the centrate clarity.

Generally speaking, the solvation power of the liquid extract of the liquefaction product at 400° F. is approximately the same as the solvation power of pyridine at room temperature, and the solvation power of the liquid extract plus the hydrocracked centrate fraction at 400° F. is approximately the same as that of MEK at room temperature. Accordingly, the solids distribution curves for pyridine insoluble solids and MEK insoluble solids in FIG. 2 may be taken as representative, respectively, of the sizes of solids in the liquefaction product in Run 1 and solids in the liquefaction product containing the hydrocracked centrate fraction in Runs 2 and 3. This indicates that the improved clarity which accompanied the indicated

and solids in the liquefaction product in Run 1 and solids in the liquefaction product containing the hydrocracked centrate fraction in Run 2 and 3. This indicates that the improved clarity which accompanied the indicated resolidification of quasi solids in Runs 2 and 3 occurs, apparently, because the resolidification increases the less than 10 micron particle sizes of at least some of the already solid particles in the liquid extract to a size greater than 10 microns, shifting these particles into a separable size range. The marked nature of the clarity improvement suggests that the addition of the hydrocracked centrate fractions in Runs 2 and 3 served to agglomerate the smaller than 10 micron particles in the liquefaction product fed to the centrifuge.

Undoubtedly, in addition to the foregoing, the reduction in specific gravity and viscosity evidenced by Table I also contributed to the increased resolution in the separation process. The viscosity figures, which were obtained in a Brookfield viscometer, cannot be regarded as quantitatively accurate at the 400° F. operating temperature. However, they can be taken as qualitatively indicative of the relative reduction in viscosity occurring with the addition of the hydrogenated centrate fraction.

Example 2, which is set out below, sheds further light on the relationship between specific gravity, ash reduction, and addition of a hydrogenated centrate fraction.

Example 2

In a continuous seven-day run, coal was liquefied and centrifuged in a solid bowl scroll discharge centrifuge operating at about 400° F., essentially under atmospheric pressure, while a coker oil fraction derived from a centrifuge underflow (as described in connection with FIG. 1) and boiling within the range of from about 100° F. and about 700° F. with 20 volume percent thereof boiling below about 400° F. was added to the centrifuge feed. In the liquefaction reactor, the conditions which produced the feed to the centrifuge included a temperature of 770° F., a pressure of 350 p.s.i.g., a 7:1 solvent/coal weight ratio of —100 mesh Illinois #6 coal in hydrogenated creosote oil boiling from about 300° F. to over 1000° F., a coal feed rate to the liquefaction reactor of 8 lbs./hr. and a 1 hour residence time. Except as indicated in FIG. 2, the feed rate of centrate coker oil fraction was about 2 lbs./hr., an addition of about 3 weight percent of centrate fraction to the centrifuge feed. The centrate rate was about 65 lbs./hr. The results of this seven-day run are displayed in FIG. 3.

FIG. 3 indicates that a monitoring of the specific gravity of the centrate provides a good measure of the how much more, or less, of coal extract liquid having at least about 20 volume percent of fractions boiling below about 400° F. needs to be added to the liquefaction product introduced to a centrifuge separation zone, in a continuous operation, in order to get and keep a desired increase in centrate clarity (reduction in ash content) as the makeup of liquefaction product varies. By controlling the addition of coker oil fraction to keep the specific gravity of the centrate, corrected to 60° F., below about 1.085 in this example, it was possible to maintain the ash content below a maximum level of about 0.3 weight percent, and, at steady state conditions, below about 0.10 weight percent, as occurred after about 60 hours of operation. As illustrated by FIG. 4, at about 90 hours the specific gravity of the centrate, corrected to 60° F., was permitted to creep over the 1.085 mark selected for the separation control in the processing of the particular slurry of this example. Addition of sufficient centrate fraction to push the specific gravity back to or below the selected mark was not made, and as illustrated, the maintenance of a uniform centrate fraction feed rate without regard to the rising centrate specific gravity permitted the ash content of the centrate to rise.

Because of the relatively higher specific gravity of the clarified liquid extract bottoms fraction boiling above

about 1000° F. and containing ash solids, the foregoing use of specific gravity measurements is not believed applicable to the bottoms fraction. The bottoms fraction with the ash solids contaminant is surprisingly effective, however, in clarifying the liquid extract, as shown by Example 3.

A solid bowl scroll discharge centrifuge was used to clarify the coal extract of a liquefaction product at a temperature of about 400° F. The ash content in the clarified coal extract was reduced from approximately 3 weight percent to about 0.15 weight percent. As illustrated in FIG. 1, the clarified centrate was then hydrocracked and fractionated. Upon commencing a recycle to the centrifuge feed of fractionator bottoms boiling above about 1000° F. and containing fine solids which had already passed through the centrifuge, approximately 25 pounds of recycle fraction being added to 81 pounds of the normal feed (about 31 weight percent), the clarity of the centrate did not deteriorate, as one would normally expect. Instead, the ash content of the centrate surprisingly decreased to approximately 0.03 weight percent.

Having now fully disclosed with particularity preferred modes by which our invention may be carried out various modifications and alterations within the spirit and scope of our invention, as claimed, will occur to those in the art.

We claim:

1. In a process of clarifying a coal liquefaction product containing solid residues in a solvent enriched by coal extract liquids, by feeding such coal liquefaction product into a solids-liquid separation zone in which solids size is a parameter of separation for separation of solid residues from the extract-enriched solvent, separated solids being discharged from the separation zone as a high solids content slurry, and the extract-enriched solvent being discharged from the separation zone as a clarified extract enriched solvent stream, the improvement which comprises:

adding to the feed to said solids-liquids separation zone a coal extract liquid derived from said coal liquefaction product and containing at least 20 volume percent of materials boiling below about 400° F., in an amount effective to increase the clarity of the clarified extract-enriched solvent stream.

2. The process of claim 1 wherein said amount is in the range from about 1 to about 50 weight percent of the resultant stream to said zone.

3. In a process of clarifying a coal liquefaction product containing solid residues in a solvent enriched by coal extract liquids, by feeding such coal liquefaction product into a solids-liquid separation zone in which solids size is a parameter of separation for separation of solid residues from the extract-enriched solvent, separated solids being discharged from the separation zone as a high solids content slurry, and the extract-enriched solvent being discharged from the separation zone as a clarified extract enriched solvent stream, the improvement which comprises:

adding to the feed to said solids-liquids separation zone a coal extract liquid derived from said coal liquefaction product and containing at least 20 volume percent of materials boiling above about 1000° F., in an amount effective to increase the clarity of the clarified extract-enriched solvent stream.

4. The process of claim 3 wherein said amount is in the range from about 1 to about 50 weight percent of the resultant stream to said zone.

5. In a process of clarifying a coal liquefaction product containing solid residues in a solvent enriched by coal extract liquids, by feeding such coal liquefaction product into a solids-liquid separation zone in which solids size is a parameter of separation for separation of solid residues from the extract-enriched solvent, separated

solids being discharged from the separation zone as a high solids content slurry, and the extract-enriched solvent being discharged from the separation zone as a clarified extract enriched solvent stream, the improvement which comprises:

adding to said coal liquefaction product a stream selected from:

(a) a fraction of said extract-enriched solvent containing at least about 20 volume percent of coal extract materials boiling below 400° F. or above about 1000° F.,

(b) a fraction of hydrocracked extract-enriched solvent containing at least about 20 volume percent hydrocracked coal extract materials boiling below about 400° F. or above about 1000° F., and

(c) a fraction of a coker oil stream containing at least about 20 volume percent of materials boiling below about 400° F. produced by coking said slurries of solid residues,

such stream being added in an amount effective to resolidify sufficient of quasi-solid materials of the coal extract to make larger and more easily separable at least a portion of the smaller, difficultly separable solids in the liquefaction product, whereby the clarity of the clarified extract enriched solvent discharged from said solids-liquids separation zone is improved.

6. The process of claim 5 wherein said stream is selected from said fractions containing at least about 20 volume percent of coal extract materials boiling below 400° F., or mixtures thereof, and said stream is added to said coal liquefaction product as necessary to keep the specific gravity of the clarified extract-enriched solvent below a selected value, the range from about 1.08 to about 1.12, at which ash content in the clarified extract-enriched solvent exceeds a desired limit.

7. The process of claim 5 in which said stream is added in amounts which constitute from about 1 to about 50 weight percent of the resultant stream to the solids-liquid separation zone.

8. The process of claim 5 in which said stream is added in amounts effective to resolidify less than about 5 weight percent of said quasi-solid materials in said coal extract.

9. The process of claim 5 in which at least a portion of solids of size smaller than about 10 microns are made larger and more easily separable on addition of said stream.

10. A method of producing a clarified coal-enriched solvent which comprises:

feeding a coal liquefaction product containing solid residues in a solvent enriched with a liquefied coal extract, into a centrifuge, at a temperature from about 300° F. to about 550° F.,

receiving the clarified overflow and the concentrated solids underflow issuing from the centrifuge,

passing the concentrated solids underflow into a coking zone operating to produce distilled products therefrom,

distilling the products from the coking zone and the clarified overflow to recover a recycle stream selected from

(a) a fraction boiling within the range from about 300° F. to about 700° F. and containing at least about 20 volume percent of liquid coal extract materials boiling below 400° F., and

(b) a fraction boiling above 1000° F. which contains ash solids, and

adding said recycle stream to said liquefaction product in amounts which constitute from about 1 to about 50 weight percent of the resulting feed to the centrifuge and which are effective to cause the

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clarity of the overflow issuing from the centrifuge to improve.

11. The method of claim 10 wherein said recycle stream is said fraction boiling within the range from 300° F. to about 700° F., and wherein said fraction is added to said liquefaction product as needed to keep the specific gravity of the clarified overflow below a selected value in the range from about 1.08 to about 1.12 at which ash content in the clarified extract-enriched solvent exceeds a desired limit.

12. The process of claim 10 wherein said recycle stream is added to said liquefaction product so as to constitute less than about 20 volume percent of the resulting feed to the centrifuge.

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DELBERT E. GANTZ, Primary Examiner

10 J. W. HELLWEGE, Assistant Examiner

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