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(54) Process for the removal of solids from an oil and mixture useful therefor.

(57) A process for removing suspended solids, particularly difficultly filterable inorganic solids, from hydrocarbon oils such as those obtained as a refinery process bottom fraction from both steam and catalytic cracking units or from coal conversion processes (e.g., coal tar) by adding to the oil an agglomerating agent comprising a mixture of a water-soluble polyelectrolyte and a water-soluble demulsifier such as an oxyalkylated phenol formaldehyde resin glycol ester whereby said solids are clustered together into readily filterable agglomerates.

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PROCESS FOR THE REMOVAL OF SOLIDS FROM AN OIL AND MIXTURES USEFUL THEREFOR

This invention is concerned generally with the removal of suspended solids from an oil. More particularly it relates to a process for producing a solids-reduced hydrocarbon oil in which suspended solids in the oil are agglomerated by adding to the oil a mixture of solids-agglomerating agents comprising a demulsifying agent and a polymer and thereafter separating the agglomerated solids from the oil.

A number of processes in petroleum production and refining, coal conversion and the chemicals industry produce as by-products liquid hydrocarbons containing insoluble solid particles oftentimes in the form of finely divided suspended inorganic solids.

Among the processes which produce liquid hydrocarbons containing appreciable amounts of finely divided suspended solids are steam cracking, catalytic cracking, coal gasification, coke production, and liquefication of coal. Steam cracking produces a steam cracking tar which contains insoluble particles of coke generally at a level of 0.001 to 5.25% with the remainder being useful heavy liquid hydrocarbons. .Catalytic cracking produces cat cracker bottoms which contain catalyst fines generally at a level of 0.1 to 5 wt. % with the remainder being useful heavy liquid hydrocarbons. Liquefication of coal, such as by the donor solvent technique as described in U.S. Patents 4,085,031; 4,253,937; 4,048,054 and 4,045,328, produces a solvent-coal slurry containing insoluble particles. Other liquids from coal are produced in its conversion processes by, for example, in its gasification, coke preparation and other processes involving the pyrolysis of coal. These liquid hydrocarbon streams contain insoluble particles which are desirably removed or reduced in level to allow for their use as a fuel oil or as a feedstock for producing other products.

These liquid hydrocarbon streams oftentimes are routed to a settling tank wherein the solid particles (catalyst fines, coke, inorganic matter, are allowed to gravity settle over an extended period of time whereby an upper layer of substantially particle-free liquid hydrocarbons can be decanted off for product use. Settling of the particles may also be provided for in intermediate or shipping tanks. Unfortunately gravity settling is too slow for the refinery, coal conversion and chemical processes now in use.

Improved techniques which are in use include electrofiltration, filtration and centrifugal separation. The latter two approaches appear to have a low capacity or throughput and a high capital cost. Electrofiltration was handicapped by lack of a regenerable filter media which is stated to have been overcome by the use of hard, smooth spherical glass beads as taught in U.S. Patents 3,799,855 and 3,799,856. Unfortunately these techniques are further limited since the typical oil-suspendible solids have average diameters of size below about 100 microns (commonly described in the art as difficultly filterable solids) which size makes satisfactory separation by mechanical separation techniques, including filtration, centrifugation and settling difficult to impossible.

Chemical treatments for oil containing suspended solids have been proposed in the art but, in general, each method suffers from some disadvantage as seen from the prior art discussion of U.S. Patent 4,094,770 wherein the patentee has taught a process for separating suspended unfilterable particulate solids from an oil by agglomerating the solids by means of an agglomerating agent comprising a mixture of acetone and 2-butanone.

In U.S. Patent 4,029,567 an agglomerating agent, especially ethanolamine is used to help separate the mineral solids and undissolved coal particles from a solution of coal liquefication products.

Gravity settling can also be enhanced by the presence of a surface-active agent as taught in U.S. 2,952,620 wherein solid particles of a silica-alumina cracking catalyst suspended in a heavy gas oil was separated from the oil by treating the suspension with an aqueous solution of a nonionic surface-active agent, e.g., a condensation product of diisobutyl phenol and 9-10 moles of ethylene oxide.

Gravity settling can be induced by use of a settling vessel in which the hydrocarbon oil containing the solids is subjected to a temperature gradient (see U.S. 4,048,063).

Japanese Published Patent Application 53-34806 of 1978 regenerates used, iron-contaminated lubricating oil by the addition of water-soluble polymers as water-in-oil emulsions to coagulate the iron whereby it becomes suitable for mechanical removal.

The dedusting of solids-containing hydrocarbon oils such as these derived from oil shale is accomplished by the use of various surface active agents (see U.S. 4,407,707).

The use of gravity settling additives and techniques have enhanced the settling rate whereby gravity settling became a feasible method for removal of suspended solids requiring little additional capital investment, a mechanically simple operation and readily modified by change of the additive.

It is the object of this invention to enhance the gravity settling rate of suspended solids from hydrocarbon oils by use of an improved agglomeration aid alone or in combination with other additives.

In accordance with the object of this invention, there is provided a process for reducing the solids content of a hydrocarbon oil fraction comprising:

providing a hydrocarbon oil fraction having a solids content greater than 0.02 weight percent and boiling in the range of from about 200°C to about 550°C;

treating said fraction with at least 10 weight parts per million of a demulsifier, preferably an oxyalkylated phenol formaldehyde resin glycol ester and at least 10 ppm of a water-soluble polyelectrolyte having a $\bar{M}w$ of from 1,000 to 25,000,000; and,

recovering a deashed hydrocarbon oil portion having a reduced ash content of filterable solids.

It has been discovered that the residual hydrocarbon oils from petroleum and coal conversion processes, for example, hydrocarbon oils boiling in the range of about 200°C to 550°C, can be readily reduced in solids, preferably inorganic solids, content to an oil having less than 500 weight parts per million (WPPM) of filterable solids when admixed with from 25 to 1000, preferably 50 to 250 ppm of a mixture of an ethoxylated-propoxylated C_4-C_9 alkyl phenol formaldehyde resin glycol ester of 2,000 to 15,000 weight average of molecular weight ($\bar{M}w$) and a water-soluble polyelectrolyte of 1,000 to 25,000,000 $\bar{M}w$ at a temperature of from 35 to 210°C and allowed to gravity settle for from 0.3 to 10 days.

The demulsifier agglomeration aid is preferably of the class of oxyalkylated phenol formaldehyde resin glycol esters of $\overline{M}w$ ranging from 500 to 50,000, preferably 2,000 to 15,000, optimally 5,000 to 8,000. The optimal is the reaction product of a phenol formaldehyde resin and propylene oxide which product is then reacted with ethylene oxide and finally esterified as by reaction with maleic anhydride or succinic anhydride, which collectively is designated herein as a succinate.

The water-soluble polyelectrolytes are macromolecular and generally of 1,000 to 25 million, preferably 10,000 to 15 million, in molecular weight and preferably of a combined water-polyelectrolyte aggregate size of 0.5 to 50 microns such as would be exhibited by water-in-oil emulsions of water-soluble vinyl addition polymers of $\overline{M}w$ ranging from 10,000 to 25 million. These polyelectrolytes include the cationic, nonionic and anionic types.

Preferred is a cationic polyelectrolyte polyamine such as a Mannich amine polymer or a partially quaternized tertiary amine polymer.

Within the steam cracking reaction or the catalytic cracking reactor, the liquid hydrocarbon feedstock is subjected to the processing conditions of elevated temperature and sometimes elevated pressure to accomplish the desired cracking. The resultant effluent of the reactor is then fractionated into the desired fractions of gases, light liquid hydrocarbons and heavy liquid hydrocarbons, with the heaviest and highest boiling fraction being the steam cracker tar or from a catalytic cracker which contain the insoluble particles. The coal liquefication process involves contacting particulate coal with a hydrogen (e.g., a hydrogen donor solvent) under liquefication conditions producing a hydrocarbon stream containing insoluble particles. The hydrocarbvon stream can be fractionated to produce gases, light liquid hydrocarbons and heavy liquid hydrocarbons with the heaviest fraction being the bottoms containing the particles. Other liquids from coal are produced by coal conversion process utilizing the pyrolysis of coal.

The gasification of low-BTU coal to supply fuel gas for boilers, kilns and process furnaces was widespread until low cost natural gas became available. The natural gas curtailments in the early 1970's along with the rapid rise in natural gas prices have reawakened interest in industrial coal gasification to provide fuel gas for kiln operations, heat treating furnaces, boilers and industrial heating. The gasification process yields a hot raw produicer gas which upon quenching yields varying amounts of coal tar. Since the coal tar has wide industrial applications both for tar-based chemical and pharmaceutical products and for fuels, it is highly desirable to reduce the inorganic ash content of these tars. Similarly, in the production of coke, the gas derived from the carbonization of the coal into coke can contain significant amounts of coal tar which is recovered and similarly processed.

Thus, this invention broadly treats any liquid hydrocarbon stream containing insoluble solids or particles, particularly fine inorganic solids and liquid hydrocarbons to remove or substantially reduce the solids content of the hydrocarbon oil and is particularly applicable to oils containing finely divided suspended solids.

Finely divided oil-suspended solids, in general, are effectively removed from the oil by the process of the invention. Those common properties which engender oil suspendability of these particles, for example, particle size, density, charge and the like, are also believed to render them susceptible to effective agglomeration and removal by the present process. Representatie solids include mineral ash-forming impurities, coal coke, carbonaceous solids, catalyst and spent shale fines, natural and synthetic mineral oxides, organic and inorganic salts and mixtures thereof and the like in particulate form and for the unfilterable solids sized in the average diameter range below about 100 microns, especially below about 60 microns.

Representative suspended-solids-containing oils suitable for use herein include shale oil, coal liquefaction oils as from extraction, hydrogenation, thermal treatment and combinations thereof, coal tars from coke manufacture, tar sand oils, petroleum refinery decant oils, oils from a fluid catalytic cracking process unit, resids, and like oils with all having less than about 10 weight percent of water.

These hydrocarbon oils are most effectively treated by the invention when the fraction treated boils in the range of 200°C to 550°C and has a total insoluble solids content greater than about

1,000 WPPM, e.g., from 1,000 to 50,000 WPPM more, normally an insoluble solids content in the range of 2,000 to 10,000 WPPM.

The Agglomeration Aid

A prime feature of the present process is the discovery of a unique solids-agglomerating agent which is enhanced in function in a hydrocarbon oil system by the presence of a water-soluble macromolecular polyelectrolyte. A solids-agglomerating additive, to be useful and effective in this service, must promote essentially complete removal of solids from an oil and at the same time must leave the oil virtually intact. In general, known solvents employed for recovering solids from an oil do not meet the latter requirement. The failure of these solvents is manifest in their inability to effectively solubilize both paraffinic-type hydrocarbons and asphaltene-type hydrocarbons. Of course, it must be apparent that the most difficultly filterable solids are the inorganic particles for which the solvent approach is of no value. In addition, an appreciable portion of the oil is usually rejected (a loss to the process of desirable product precursors) in the form of tacky or flocculent solids.

It has been discovered that the introduction of a mixture of a polyelectrolyte such as a cationic polyamine polymer, and an oxyalkylated alkyl phenol formaldehyde glycol resin ester of $\overline{M}w$ ranging from 500 to 50,000, preferably 2,000 to 15,000, optimally from 5,000 to 8,000, into a solids containing hydrocarbon oil in amounts ranging from 10 to 1,000, preferably 25 to 250, ppm based on the weight of said oil markedly enhances the gravity settling of said solids so that in from 0.3 to 10 days the solids content of said oil is reduced to less than about 500 WPPM. Preferred for use as a demulsifier agglomeration aid is an ethoxylated propoxylated C_4-C_9 alkyl phenol formaldehyde resin ester of a C_4-C_{10} dicarboxylic acid anhydride, e.g., maleic or succinic anhydride, admixed with an equal weight amount of a Mannich amine polyelectrolyte such as a condensation product of polyacrylamide, formaldehyde and dimethylamine.

These demulsifiers useful in the process of this invention include both water and oil soluble products. They are well known in the art, and include, for example, oxyalkylated amines, alkylaryl sulfonic acid and salts thereof, oxyalkylated phenolic resins, polymeric amines, glycol resin esters, polyoxyalkylated glycol esters, fatty acid esters, oxyalkylated polyols, low molecular weight oxyalkylated resins, bisphenol glycol ethers and esters and polyoxyalkylene glycols. This enumeration is, of course, not exhaustive and other demulsifying agents or mixtures thereof will occur to one skilled in the art. Most demulsifiers which are commercially available fall into chemical classifications such as those enumerated above in which the $\overline{M}w$ generally ranges from 500 to 50,000.

The preferred demulsifiers for this invention, glycol resin esters are derived from alkyl phenol formaldehyde resins having molecular weights of 500 to 50,000 which are alkoxylated and thereafter esterified by reaction with an ethyleneically unsaturated dicarboxylic acid or anhydride such as maleic anhydride. Such glycol resin esters are typified by an oxyalkylated C_4-C_9 alkyl phenol formaldehyde glycol resin esters having a $\overline{M}w$ within the range of 500 to 50,000, preferably 2,000 to 15,000.

The bisphenol glycol ethers and esters are obtained by the alkoxylation of bisphenol A to molecular weights of from 3,000 to 5,000 and for the esters the ether products are esterified by reaction with organic acids such as adipic, acetic, oxalic, benzoic, and succinic including maleic anhydride.

The salts of alkyl aryl sulfonic acids include those of ammonium, sodium, calcium, and lithium. The useful alkyl aryl sulfonic acids can be obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as, for example, those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from about 3 to about 15, preferably 9-12, carbon atoms. Preferred sulfonic acids are those obtained by the sulfonation of hydrocarbons prepared by the alkylation of benzene or toluene. The alkaryl sulfonates contain from 7-21 carbon atoms, preferably from 15-18 carbon atoms per alkyl substituted aromatic moiety.

Oxyalkylated amines are represented by the ethylene oxide, propylene oxide and mixtures of ethylene/butylene oxides derivatives of organic amines such as ethylene diamine, ethyl amine, propyl amine, aniline and alkylene polyamines.

Polyelectrolytes as used herein refer to a polymer water-soluble or water-dispersible which contains polyions. The polyelectrolytes have molecular weights ranging from 1,000 to 25 million with those having ($\overline{M}w$)'s in excess of 0.5 million preferred.

For use in this invention, the polyelectrolyte may be either cationic or anionic and, in some instances, the ionic charges are sufficiently slight so that the polymers may be considered as nonionic. For example, water-soluble polymers and copolymers of allyl, dially amines, or dimethylaminoethylmethacrylate are cationic. Polymers such as polyvinyl alcohol are nonionic, and polymers such as polyacrylic acid or polystyrene sulfonates are anionic. All of these polymers are considered useful polyelectrolytes and may be used in the practice of the invention.

The molecular weight of the polyelectrolytes described above may vary over a wide range, e.g., 1,000-25,000,000, although it is preferred to use nitrogen containing (such as acrylamide) polymers whose molecular weights are in excess of 1,000,000. These polyelectrolytes are well known and generally available as articles of commerce. Thus those polyelectrolytes which have utility in combination with the water-soluble demulsifying agents such as the alkoxylated esters according to the process of this invention include:

(a) cationic types such as:
  polymerized esters and amides of acrylic or methacrylic acid, that contain pendant cationic funtionalities;
  quaternized a partially quarternized Mannich amines;
  polymers of mono or dialkyl diallyl ammonium salts, or of substituted analogs thereof, or their copolymers with nonionic monomers such as acrylamide;
  quaternized oxyalkylated polyamines;
  quaternized polyalkylene polyamines;
  dialkylamine halohydrin copolymers; and,
  dialkylamine polymethylenedihalide copolymers (a.k.a. ionenes);

(b) nonionic types such as:
- acrylamide polymers;
- polymers of glycol esters of acrylic or methacrylic acid;
- polyoxyethylene, polyoxyalkylenes, or copolymers thereof;
- polyvinylalcohol, or oxyalkylates or esters thereof;
- polyalkylene polyamines, such as tetraethylene pentamine;
- polyoxyalkylated polyamines;
- polysaccharides, celluloses, or chemical modifications thereof, such as carboxymethylates or hydroxyethylates;
- Mannich amine condensation polymers; and,
- melamine formaldehyde condensation polymers;

(c) anionic types such as:
- partially hydrolyzed polyacrylamide;
- polyacrylic or polymethacrylic acid (sodium or other salt);
- sulfonated polystyrene, sulfonated polyalkylstyrene, or copolymers thereof (sodium or other salt); and,

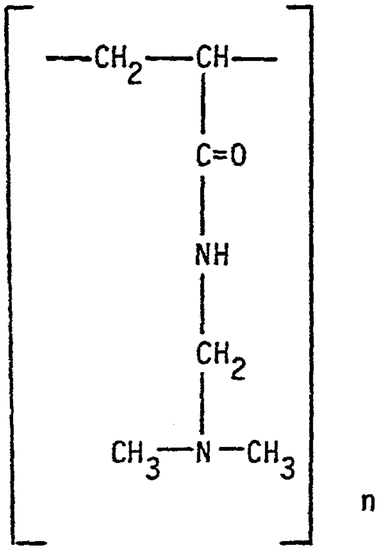
(d) polyampholytes and polybetaines.

One class of preferred polyelectrolytes are the water-soluble vinyl addition polymers which are well known in the art, widely described in the literature, and generally commercially available as water-in-oil emulsions. The emulsion type polymers most commonly used in industrial applications are acrylamide polymers which include polyacrylamide and its water-soluble copolymeric derivatives such as, for instance, acrylamide-acrylic acid, and acrylamide-acrylic acid salt copolymers which contain from about 95-5% by weight of acrylamide. Also useful are copolymers of acrylamide with other vinyl monomers such as maleic anhydride, acrylonitrile, styrene and the like. Other water-soluble vinyl polymers are described in detail in the following U.S. Patent Nos.: 3,418,237, 3,259,570 and 3,171,805. These polymers may be produced by any known method of conducting polymerization reactions. Thus, solution, suspension or emulsion polymerization techniques may be used. The emulsion polymerization generally produces polymers or gums having concentrations within the range of 0.1 to 20% by weight. The aqueous solutions of polymers have a solution concentration of 0.2-2.0% by weight.

The water-in-oil emulsions generally contain oil to water weight range of 5:1 to 1:10 with preferred emulsions being prepared in the ratio of 2:1 to 1:10. The aggregate polymer-water gel-like particle in the water-in-oil emulsion ranges from 0.5 to 50 microns in diameter.

Particularly useful commercially available representatives of this class are partially quaternized amine polymers consisting of complex structures of 1°, 2° and 3° amines, and optionally epi-chloro-hydrin.

Another class of particularly useful polyelectrolytes are the water-soluble Mannich amine polymers of the general formula



$$\left[-CH_2-CH(-C(=O)-NH-CH_2-N(CH_3)-CH_3)- \right]_n$$

of which a commercial representative is Jayfloc® 854 solid by Exxon Chemical Americas of Houston, Texas.

In the admixture the weight ratio of demulsifier to polyelectrolyte ranges from 0.5:99.5 to 99.5:0.5, preferably 1:4 to 4:1, optimally 1:2 to 2:1.

In the event that the solids-containing hydrocarbon contains from 0.05 to 10 weight percent of water, it is useful to supplement the agglomeration aid with from 0.5 to 5 parts by weight of a water shedding additive for each part by weight of said agglomeration aid mixture. Since the water may provoke foaming, silicone defoamants may be also added as well as other nonionic and anionic surfactants.

All $\bar{M}w$ given herein are weight average molecular weights as determined by gel permeation chromatography or light scattering as appropriate.

Agglomeration Conditions

Agglomeration conditions for use in the process of the invention will vary depending upon such process factors as the type and solids content of the hydrocarbon oil, the size distribution of the solids and the properties of the oil being processed. In general, the most satisfactory process temperature will range from 35°C to 250°C, preferably from 50°C to 225°C and optimally from 75°C to 210°C. In general the process residence time required to reach the desired ash level of less than 0.05 weight percent will range broadly from 0.3 to 10, more usually 2 to 5, days.

The agglomeration aid and, if desired, the supplemental additives such as a water deshedding aid are introduced into the hydrocarbon oil stream to be treated prior to or at the point at which said stream is introduced into the top of the settling tank. The product of the process is withdrawn from a point intermediate (on the side) while the solids settle by gravity to the bottom of the tank. The flow rates and unit sizings in the process system are adjusted to provide the desired residence time in the settling tank. The settled solids in the settling tank are withdrawn generally as a sludge for direct disposal or further treatment to recover additional hydrocarbon oil.

The following examples are provided to illustrate the embodiments of the invention and are not intended to limit it in any way.

Examples 1-14

In each of these, hydrocarbon oil bottom fractions (obtained from four different refineries) having suspended solids with the following general physical characteristics were used:

Table 1

Physical Characteristics	
Viscosity cst at 210°F	8-10
Ash content, wt. %	0.01-0.02
Coking value, wt. %	6.5-7.2
Asphaltene (n-heptane insolubles), %	0.5-1.5
Toluene insolubles (0.35), %	0.1-0.2
Number average mol. wt.	250-300
Filterable solids (WPPM)	1,000-50,000

The hydrocarbon oil bottom fraction obtained from the refinery was charged into a kilogram glass reactor which was electrically heated and equipped with a mechanical agitator. The 200 ml charge of oil was pretreated by heating to 80°C prior to admixture with a blend containing the indicated agglomeration aid at a blend treat rate of 500 ppm for the oils from Refineries Nos. 1-3 and at both 100 and 200 ppm for the oil from Refinery No. 4. The treated charge was allowed to agitate for 2 minutes and then settle for 72 hours while holding the temperature at 79°C, thereafter 50 ml was drawn off from the upper region of the reactor and subjected to filtration to determine the filterable solids in weight parts per million (WPPM) according to the following technique.

The 50 ml sample is weighed as is the filter paper (0.8 microns pore size) used for the test. The sample is preheated to 70-80°C, then mixed with 150 to 200 ml of hot xylene (heated above 55°C) and the admixture poured into the vacuum filter. The container and filter paper are fully rinsed with hot xylene and thereafter with heptane. The now fully rinsed paper is dried at 82°C for 30 minutes and then placed in a desicator for 30 minutes. The weight of the solids found on the filter paper provides the means for measuring the weight parts per million (WPPM) of filterable solids of the original sample.

The sample obtained from a refinery was treated according to the process of this invention using mixtures containing various polyelectrolytes all of which are commercially available and the results compared with that of the same process using several other polyelectrolyte additives. The results are set forth in Table II.

The invention in its broader aspect is not limited to the specific details shown and described and departures may be made from such details without departing from the principles of the invention and without sacrificing its chief advantages.

Table II

Example	Additive	Treat Rate ppm	Solids Recovered (avg. 2 runs) wppm
1	Alkoxylated Resin Ester[1]	25	703
2	Mannich Amine[2]	6	633
3	Polyamine[3]	35	806
4	Alkoxylated Resin Ester[1] Anionic Polyacrylamide[4]	13 15	737
5	Alkoxylated Resin Ester[1] Cationic Polyacrylamide[5]	13 10	629
6	Alkoxylated Resin Ester[1] MFCC[6]	13 27	673
7	Alkoxylated Resin Ester[1] Cationic Copolymer[7]	13 12	648
8	Alkoxylated Resin Ester[1] Cationic Polymer[8]	13 28	856
9	Alkoxylated Resin Ester[1] Mannich Amine[2]	13 13	540
10	Alkoxylated Resin Ester[1] Mannich Amine[2]	13 6	413
11	Alkoxylated Resin Ester[1] Cationic Copolymer[9]	13 28	609
12	Alkoxylated Resin Ester[1] Polyamine[3]	13 21	560
13	Alkoxylated Resin Ester[1] Polyamine[3]	13 35	423
14	No Additive	-0-	1045

(continued next page)

Table II (cont.)

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1 represents an ethoxylated propoxylated C_9 alkylphenol formaldehyde glycol resin ester of 5,000 to 8,000 $\overline{M}w$.

2 represents Mannich amine polymer condensation product of polyacrylamide, formaldehyde and dimethylamine.

3 represents an epichlorohydrin polyamine of high charge density.

4 represents anionic polyacrylamide inverse emulsion polymer of medium charge density and $\overline{M}w$ of 15 million.

5 represents a cationic polyacrylamide inverse emulsion acrylamide copolymer.

6 represents melamine formaldehyde cationic colloids.

7 represents high charge density cationic copolymer of epichlorohydrin and dimethylamine.

8 represents represents a cationic polymer of dimethyldiallylammonium chloride of $\overline{M}w$ ranging from 100,000 to 500,000.

9 represents a cationic copolymer of acrylamide and dimethyldiallylammonium chloride.

CLAIMS:

1. A process for reducing the particulate solids content of a hydrocarbon oil fraction comprising:

providing a hydrocarbon oil fraction containing less than 10 weight percent water;

treating said .hydrocarbon oil fraction with at least a solids agglomerating amount of an agglomeration aid mixture treating being in the amount of from 10 to 1000 weight parts per million of said aid based on the weight of said fraction, said mixture comprising a demulsifying agent and a polyelectrolyte of $\bar{M}w$ ranging from 1,000 to 25,000,000; and,

recovering a hydrocarbon oil fractions having a reduced content of solids.

2. The process of claim 1 wherein said fraction had a boiling range of from about 200°C to about 550°C and at least 1000 weight parts per million (WPPM) of filterable solids, and said recovered portion had less than 500 WPPM of said mixture.

3. The process of claim 1 or 2 wherein said demulsifier is an oxyalkylated phenol formaldehyde resin glycol ester mixture.

4. The process of claim 3 wherein said ester is an ethoxylated-propoxylated C_4-C_9 alkyl phenol formaldehyde resin glycol ester of a $\bar{M}w$ ranging from 2,000 to 15,000.

5. The process of claim 3 wherein said ester is a succinate and present in said agglomeration aid mixture in from 10 to 250 ppm.

6. The process of any preceding claim wherein said treating is at a temperature of from 35°C to 250°C and for residence times ranging from 0.3 to 10 days.

7. The process of any preceding claim wherein said agglomeration aid mixture contains from 5 to 95 weight per cent of a Mannich amine polymer condensation product of acrylamide, formaldehyde, and dimethylamine.

8. The process of any of claims 1 - 6 wherein said mixture contains from 5 to 95 weight per cent of epichlorohydrin polyamine of high charge density.

9. An agglomeration agent useful for treating dry hydrocarbon oil fractions containing inorganic solids comprising a water-soluble polyelectrolyte and a demulsifier.

10. The agglomeration agent of claim 11 wherein said demulsifier is an oxyalkylated phenol formaldehyde resin glycol ester of $\overline{M}w$ ranging from 500 to 50,000 and said polyelectrolyte is in the form of polymer-water gel-like particles.