

3,108,944

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ATTORNEYS

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3,108,944

DEWAXING PROCESS

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Filed July 12, 1960, Ser. No. 42,367

3 Claims. (Cl. 203—33)

This invention relates to dewaxing hydrocarbon oils. In one aspect, the invention relates to an improved process for the dewaxing of oils. In another aspect, the invention relates to the utilization of an additive compound in a dewaxing system. In still another aspect, the invention relates to the utilization of a pour-point depressant in the reclaimed solvent in a dewaxing operation. In a further aspect, the invention relates to the operation of a dewaxing system at lower temperatures without plugging the solvent cooler by adding a pour-point depressant to the solvent prior to the cooling of the solvent.

In the solvent dewaxing of hydrocarbon oils, a diluent material is added to the waxy oil, and the solution is then chilled to a temperature at which the wax or a substantial portion thereof is precipitated. The wax is then separated from the oil by filtration, centrifuging or the like. In certain of the methods, known as solvent dewaxing methods, a solvent which has a preferential solvent action for oil over wax at low temperatures, is utilized as the diluent. Solvents which can be utilized include naphthas, ketones such as methyl-ethyl ketone, acetone-benzol mixtures, acetone-toluene mixtures, liquid paraffins of low boiling point such as propane, butane, pentane, and hexane, and chlorinated hydrocarbons such as dichloroethane and trichloroethylene. These solvents, being very fluid at low temperatures, reduce the viscosity of the oil to such an extent that low temperatures can be obtained during the precipitation process, and as a result low pour-point oils can be obtained.

In the operation of dewaxing systems, the quantity of wax extracted is directly governed by the temperature to which the wax-bearing stock is cooled, that is, the colder the temperature the more wax is precipitated from the solution. However, there are certain limitations controlling the coldest temperature obtainable. In the solvent dewaxing of certain crudes, such as Venezuelan crude, there is a tendency for the solvent cooler to become plugged, the exchangers to become fouled resulting in increased pressure drop across the exchangers, and the time required for filtration to be increased. The lower limits on temperature on the scraped surface exchanger product slurry have been 30–35° F. as lower temperatures increase the pressure drop across the exchanger and force a shutdown for dewaxing of the exchanger. In certain operations, the solvent which is recycled from the oily filtrate and finished wax strippers, contains a small amount (about 6 percent) light wax which is carried overhead with the solvent in the stripping operation, since perfect fractionation is not obtained and would require considerably more expensive fractionation equipment. It is the precipitation of the light wax in the solvent which plugs the solvent cooler, thus limiting the total cooling of the system and hampers the operation of the exchangers and the filters.

I have found that these difficulties can be reduced or eliminated and the dewaxing operation carried out at lower temperatures than previously obtainable by the addition of a pour-point depressant to the reclaimed solvent prior to cooling the solvent.

Accordingly, it is an object of the present invention to overcome the aforementioned difficulties present in the dewaxing operations. Another object of the present invention is to prevent plugging of the solvent cooler. A further object of the present invention is to prevent foul-

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ing of the exchangers. A still further object of the present invention is to decrease the time required for filtration. Yet another object of the present invention is to enable the dewaxing operations to be carried out at lower temperatures. Still another object of the present invention is to provide for more efficient utilization of the cooling capacity of the dewaxing system. Another object of the present invention is to increase the yield in a dewaxing operation. Another object of the present invention is to improve the operation of the wax filters.

Other aspects, objects, and advantages of the present invention will become apparent upon a consideration of the disclosure, the drawing, and the appended claims.

According to the present invention there is provided an improved method of solvent dewaxing of hydrocarbon oils comprising adding a pour-point depressant to the reclaimed solvent prior to cooling the solvent.

FIGURE 1 is a diagrammatic flow sheet of a dewaxing system embodying the present invention.

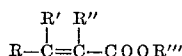
Wax distillate charge and solvent are fed to a scraped surface exchanger 3 through lines 1 and 2, respectively. The solution is chilled in exchanger 3 and passed to exchanger 4 through line 9 for additional chilling. Exchangers 3 and 4 can be double pipe chillers which consist of an inner pipe jacketed by an outer pipe of larger diameter. Inside of each of the inner pipes is a screw-like scraper composed of a central shaft with a helical scrape blade attached thereto. The scraper is rotated during the chilling operation, the blade of the scraper contacting the inner surface of the pipe to remove any adhering solid matter therefrom and force the same out of the pipe. A cooling medium is introduced into exchangers 3 and 4 by pipes 5 and 6, respectively, circulated between the two pipes of the exchangers, thus chilling the surface of the inner pipes through which the oil-solvent mixture is passed, and removed from exchangers 3 and 4 by pipes 7 and 8, respectively. It is to be understood that the two heat exchangers 3 and 4 in the drawing are symbolic of groups of heat exchangers, perhaps as many as 25 exchangers in a group, and therefore the coolant streams represented by 5 and 7, 6 and 8 are applied in countercurrent fashion to the groups of exchangers in series. A cooling medium, such as brine solution or the like can be utilized for both exchangers 3 and 4, but it is preferred to utilize the oily filtrate obtained from the filtering operations as the cooling medium for exchanger 3 to provide efficient utilization of the cooling capacity of the system, while brine solution is used as the cooling medium for exchanger 4.

The chilled solution of wax distillate and solvent is removed from exchanger 4 through line 10 where it is mixed with oily filtrate from line 24, and passed to filter 11. Filters 11, 12, and 13, which can be any type desired, such as for example rotary filters, are operated in series, the cake produced in filter 11 being passed through line 15 where it is mixed with solvent from line 16, and into filter 12, while the cake produced in filter 12 is passed through line 17 where it is mixed with solvent from line 18, and into filter 13. The filter cake produced in the final filter 13 is removed and passed through line 19 to stripping and molding operations (not shown).

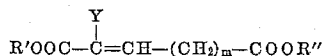
The oily filtrate obtained in filter 13 is removed through line 20. A portion of this oily filtrate is separated into line 21 and passed to filters 11 and 12 through lines 22 and 23, respectively, as a wash. The remaining portion of this oily filtrate is passed through line 24 to line 9 where it is mixed with the chilled solution of wax distillate and solvent. The oily filtrate from filters 11 and 12 is collected in pipes 25 and 26, respectively, and passed through line 5 into and through exchanger 3 as the cooling medium therefor. The solvent which is recovered in the stripping operations is returned through

line 30 where it is mixed with pour point depressant from line 31 and a portion thereof passed to solvent cooler 32. Another portion of this stripped solvent is passed via line 2 and mixed with the wax distillate charge. If desired, additional pour point depressant may be added to this latter stream at 37, if a higher concentration of pour point depressant is desired in the wax removal process than is required in the solvent cooler. A suitable cooling medium, such as brine solution or the like, is passed through line 33 into and through solvent cooler 32 and removed through line 34. A portion of the chilled solvent is removed through line 35 to filter 13 as a wash, while the remainder of the chilled solvent is fed to lines 16 and 18. Make-up solvent may be added at 36, as required.

Some pour point depressants which can be used to advantage in the present invention are Paraflow, Acryloid-150 and Santopour. Paraflow and Acryloid-150 are considered to be included among the compositions which are described in U.S. Patent 2,798,027 as component A and component B, respectively. In said patent, component A is described as a Friedel-Crafts condensation product of a halogenated paraffin and aromatic hydrocarbon containing a maximum of three substituent groups and/or condensed rings. The aromatic compound may be a hydroxyl compound such as phenol, cresol or xylene, or an amine such as aniline, but is preferably naphthalene, phenanthrene or anthracene. The halogen-bearing paraffinic substance may be a chlorinated paraffin wax containing, for example, from 10 to 20 percent by weight of chlorine. Acid chlorides containing at least 10 carbon atoms per molecule may also be used, as also may chlorinated alcohols, ethers or esters. The preferred chlorine content is from 10 to 20 percent by weight. Also, in said patent compound B is described as polymeric compound formed by polymerizing (a) a compound of general formula:



wherein R is hydrogen or an alkyl radical, R' is hydrogen or a halogen atom, R'' is hydrogen, a halogen atom, or an alkyl radical, and R''' is an alkyl, aralkyl, or alicyclic radical having not less than eight carbon atoms. When R and R'' are both alkyl radicals then it is preferred that they each contain not more than 5 carbon atoms. Examples include acrylic, methacrylic, alphachloroacrylic, crotonic, alpha-chlorocrotonic acids and mixtures of these; or (b) esters of alpha-beta-unsaturated dicarboxylic acids with either vinyl acetate or styrene. Examples include Lorol fumarate copolymerized with either vinyl acetate or styrene; or (c) esters formed from alpha-beta unsaturated carboxylic acids and C₆ to C₁₈ preferably C₁₀ to C₁₅ alcohols; or (d) esters of general formula:



wherein Y is hydrogen or methyl, m is equal to zero or 1, and R' and R'' are alkyl groups preferably having from 6 to 18, preferably 10 to 15 carbon atoms. Examples include esters of maleic, fumaric, glutaric, alpha-methyl glutaric, mesaconic and citraconic acids. Santopour is a pour point depressant for lube oil manufactured by the Monsanto Chemical Company, exhibiting API gravity of 29.5°, flash point of 400° F., pour point of 10° F., and viscosity of 60 SUS at 210° F.

With the pour point depressant "Paraflow," for example the concentration range in the solvent stream should be from 0.001 to 0.010 percent, and preferably from 0.003 to 0.005 percent. Other pour point depressants will vary somewhat in effectiveness, but should be in this same general range.

In an experimental run, apparatus as shown in the draw-

ing was operated with a wax distillate containing 30 percent wax, a naphtha solvent, and "Paraflow" as the pour point depressant. The heat exchanger 3 of the drawing represents twenty units operated in series with the oily filtrate 5 sent through the cooling jackets in countercurrent flow to the charge stock, and exchanger 4 represents ten units operated in similar fashion. Experimental conditions within the system are given in the following table.

TABLE

Experimental Conditions of Operation

Drawing Designation	Temperature, ° F.	Wax, gal./hr.	Solvent, gal./hr.	Oil, gal./hr.	Brine, gal./hr.	Additive, gal./hr.
1	90	350		650		
2	90	12	200			0.12
5	32	156	1,283	550		
6	20				2,000	
7	90	156	1,283	550		
8	30				2,000	
9		350	200	650		
10		1593	200	650		
15		1593	997			
16	30	36	600			
17		1409	1,016			
18	30	36	600			
19		341	194			
20		168	1,007			
21		134	503			
22		117	251			
23		117	252			
24		134	504			
25			467	407		
26		140	816	144		
30		108	1,800			
31						0.40
33	20				1,000	
34	30				1,000	
35	30	24	400			
36			200			
37						

35 ¹ Contaminated with oil.

An advantage which accompanies the present invention is the triple utilization of the pour point depressant, in the solvent cooling system, in the dewaxing operations, and in the oil product. It is desirable in many instances that the oil product have the improved characteristics which are given to it by the addition of a pour point depressant, and in the present invention the pour point depressant is removed from the system as a component of the oil product, thus reducing, if not eliminating, the requirement of adding the pour point depressant to the oil product.

As noted above, the drawing is merely diagrammatic and is not intended to fully show all component parts of equipment which one skilled in the art will routinely design for the operation. Indeed, the showing of an element or piece of equipment does not mean that all such or similar pieces of equipment which may or can be designed by one skilled in the art in possession of this disclosure cannot be utilized in substitution therefor, likewise the omission of an element which one skilled in the art may include in an actual unit does not mean that such a piece of equipment is intended to be omitted simply because it does not appear in the drawing. Suffice to say, the drawing is for illustrative purposes as is the description thereof.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, the drawing, and the appended claims to the invention, the essence of which is that a pour point depressant is added to the recycled solvent prior to cooling such solvent.

I claim:

1. A method of dewaxing a wax-bearing oil stock comprising mixing the wax-bearing oil with a dewaxing solvent, chilling the solution thus obtained to a temperature sufficiently low to precipitate a substantial portion of the wax contained therein, filtering the resulting mixture in a first filtering zone to remove the precipitated wax as a first filter cake and to produce a dewaxed filtrate, admixing said filter cake with cooled solvent and passing the admixture thus obtained into a second filtering zone to produce a second filter cake and a dewaxed filtrate, re-

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covering the retained solvent from said second filter cake, the thus recovered solvent containing a small amount of light wax, mixing with said recovered solvent a pour point depressant in such amount as to substantially prevent the precipitation of said light wax when cooling said recovered solvent to a desirable temperature, passing the resulting mixture of recovered solvent and pour point depressant into heat exchanging relationship with a cooling medium to cool said recovered solvent to a temperature lower than that previously obtainable without the addition of said pour point depressant due to the precipitation of said light wax, and recycling the thus cooled solvent directly to the step of admixing said first filter cake with cooled solvent.

2. A method in accordance with claim 1 wherein said wax-bearing oil stock is a Venezuelan crude.

3. A method in accordance with claim 1 wherein said solvent is naphtha.

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