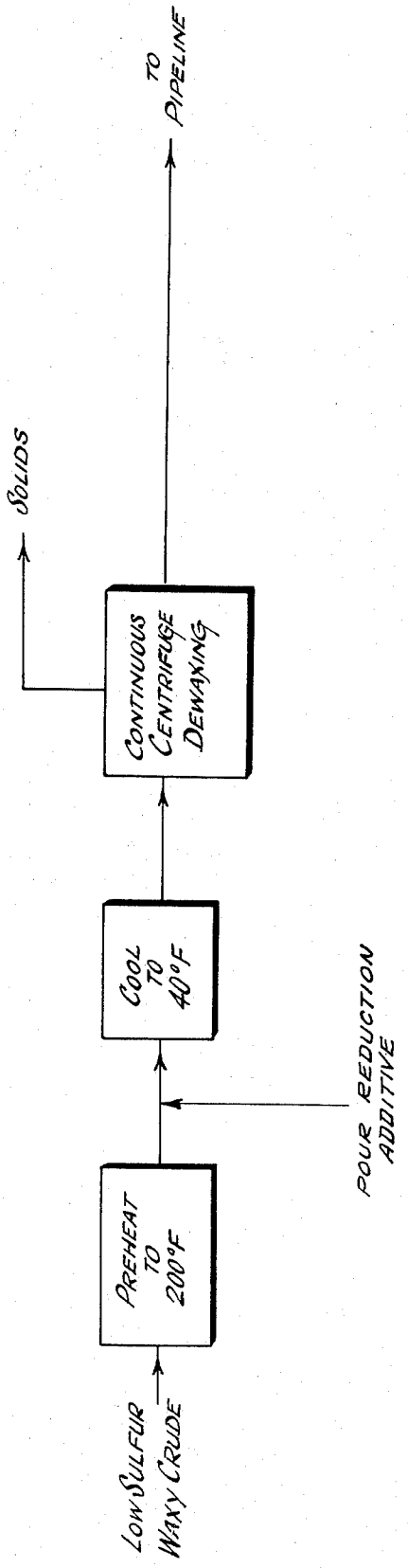
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PROCESS FOR IMPROVING THE GEL STRENGTH AND FLOW PROPERTIES OF CRUDE OIL

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ABSTRACT OF THE DISCLOSURE

The pipeline flow characteristics and the gel strength of waxy crudes, in particular North African crudes, are improved by centrifuging under specific conditions to remove an optimum amount of wax. In a modification of the process, less than the optimum of wax is removed and a dewaxing aid is added to the crude prior to centrifuging or to the dewaxed crude. The removed wax can be visbroken or thermally cracked, and the resulting fluid can be added to the dewaxed oil.

BACKGROUND OF THE INVENTION

The present invention relates to a process for improving the gel strength and pipeline flow properties of waxy crude oils.

Certain waxy, low sulfur, high pour crudes are known to have poor pipeline flow characteristics as well as a tendency to gel at temperatures near their upper pour points. This tendency is particularly troublesome when a pipeline containing these crudes is shut down under low ambient temperatures. With particular reference to the Trans Alpine Pipeline which moves North African waxy crudes, the authorities in charge (TAL) have set up specifications for waxy crudes to protect against pipeline freeze-up caused by mandatory or emergency shutdowns under European winter condtions. Those crudes which fail TAL specifications are segregated from other crudes. One of the critical TAL specifications is the "gel strength" or yield-stress value of the crude—a measure of the stress or amount of energy required to initiate flow of a gelled waxy crude. Many waxy crudes and mixtures thereof with other crudes fail to pass the minimum requirements which are set at 80 dynes/cm.^{2} at 32° F. in a ¼ inch pipeline.

Heretofore, in dealing with such flow problems, the pour point of waxy crudes has been improved mainly by the removal of wax by solvent extraction at low temperatures with the attendant expense of recovering the solvent and of providing the indicated cooling. In newer processes, wax has been removed without the use of a solvent by centrifuging a previously heated crude which has been cooled at a critically controlled and slow rate from its cloud point to a centrifuging temperature of around 35° to 55° F. Here, however, cooling at too rapid a rate causes the wax to precipitate in fine crystals which do not agglomerate with pour inhibitors such as asphaltenes and resins present in the crude.

Unexpectedly, it has been discovered in accordance with the present invention that the flow characteristics and the gel strength of waxy crude oils can be improved by centrifuging the crude oils to remove an optimum amount of wax therefrom.

In a modification of the invention waxy crudes are centrifuge dewaxed in the presence of a dewaxing agent.

In a further modification, a dewaxing agent is added to an oil which has only been partially dewaxed by centrifuging.

All the modifications of the invention result in a crude oil which passes TAL specifications.

In the practice of the present invention, a waxy crude oil is preheated to a temperature ranging from about 160° to about 200° F. and is then cooled to a centrifuging temperature of around 40° to 60° F. The crude is then centrifuged at a centrifugal force of at least 18,000 g. and preferably over 14,000 g. Single or multiple stage centrifuging can be used depending upon whether a dewaxing agent is used or not in the centrifuging stage or is added to the dewaxed oil. If no dewaxing agent is used, multiple stage centrifuging normally is preferred since at least 50% of the total wax must be removed from the crude oil to pass TAL specifications.

With the present process, the pour point of waxy crudes can be reduced by 20° to 25° F. without reversion upon prolonged storage. Relatively simple apparatus is required to carry out the process and no solvents are needed. The crudes which can be treated by the process are Arabian crudes, Amna crudes, Nafoora, Amna-Arabian blends and Nafoora-Arabian blends. The wax can be visbroken by heating under pressure to at least 800° F. in the presence of hydrogen.

As shown in the accompanying schematic drawing, the crude is initially preheated to a temperature of between 160° to 200° F. followed by cooling to centrifuge temperature. This temperature range should be respected as, for example, preheating Amna crude to 150° F. and cooling to 60° F. prior to dewaxing was found to give a gelled crude which could not be centrifuged. Variation in the mode of cooling after preheating was also investigated. No significant effect upon the gel strength properties of the dewaxed crudes was noted by cooling under static conditions, i.e. in the container as opposed to stirring.

Unexpectedly in the light of previous research by others skilled in this art, the rate of cooling to centrifuge temperature also was not found to be critical and indeed it was determined that cooling ranges of from 0.5° F. to 4.0° F. per minute gave substantially the same results.

Introduction of 0.005 to 0.05 weight percent of a dewaxing aid in the crude prior to dewaxing makes it possible to obtain the desired characteristics in the dewaxed crude without removing as much wax as is necessary in the absence of such addition. Dewaxed crude having the desired properties can also be obtained by adding the dewaxing aid to the dewaxed oil after centrifuging. Many dewaxing aids and pour point depressants will suggest themselves to those skilled in the art for use in conjunction with the manipulative steps of this invention. Among these may be mentioned acrylates, polymethacrylates, ethylene-maleic anhydride copolymers and diesters of such copolymers with predominantly straight chained alcohols having a carbon content ranging from C_{18} to C_{26}.

Particularly suitable dewaxing aids include ethylene-vinyl fatty acid ester copolymers having a vinyl fatty acid ester (C_2–C_6) content of about 24 to 34 weight percent, a melt index of from 5 to 465, and a Number Average Molecular Weight of about 20,000 to 31,000 as determined by the Membrane Osmometry analytical method, this method having a precision of plus or minus 5% at the 25,000 level.

The characterization of the various "Elvax" copolymers is given in Table I below.

TABLE I

Elvax	Percent vinyl acetate in copolymer	Melt index [1]
150	32-34	22-28
210	27-29	335-465
220	27-29	125-175
240	27-29	22-28
250	27-29	12-18
260	27-29	5-7
310	24-26	335-465
350	24-26	16-22
360	24-26	1.6-2.4

[1] In g./10 min. as determined by ASTM D 1328 modified.

The above copolymers can be added to the oils in the form of a hydrocarbon solution concentrate in, for example, toluene.

The copolymers can be prepared by any convenient process, such as that of U.S. Patent 3,215,678, which involves the free radical-initiated polymerization of ethylene and a vinyl ester of a lower saturated monobasic aliphatic carboxylic acid.

It has been noted that at higher concentrations of 0.05 weight percent, the above copolymers act both as dewaxing aids and as crude pour point depressants since 40 to 80 percent of the additive (basis infrared analysis) is carried over into the dewaxed oil.

In the present process, centrifuging can be effected in continuous or semi-continuous fashion. Generally, the dewaxed oil is continuously discharged from the centrifuge but the separated solids are recovered at the end of the run. Residence times of about 10 to 60 seconds in the centrifuge are used. A commercial centrifuge such as the Sharples Super Centrifuge can obtain a 1 to 15% separation of wax based on weight of crude. As regards centrifuging conditions in the present process a force of between about 8,000 and 15,000 *g*'s is preferred.

Following treatment by the present process, the treated crude is evaluated as to its gel strength (GS) by the following test:

A 4 oz. bottle (approximaely 1.5" by 1.5" square, with a screw cap) containing 1.5 to 2 inches of crude, tightly capped, is placed in a refrigerator at about 77° F. The air in the refrigerator is then cooled at the rate of 12° F./hr. (±0.5° F./hr.) to the test temperature, normally 32° F. or 50° F. The bottle is allowed to remain in the refrigerator for at least 1 hour after the air temperature reaches the test temperature. The bottle is then gently removed and slowly tilted to the horizontal position. If no flow occurs within 10 seconds after reaching the horizontal position, the bottle is placed in the bumping apparatus, and bumped in the horizontal position up to three times. The bumping apparatus consists of a swinging arm in which the bottle is clamped. The arm holding the bottle is raised to 15 deg. from the horizontal and dropped for the first bump, raised to 30 deg. and dropped for the second bump, and raised to 85 deg. and dropped for the third bump. The possible observations are:

(1) Flow occurs immediately upon tilting the bottle;
(2) Flow occurs only after the bottle is tilted significantly away from the vertical position but before reaching the horizontal position;
(3) Flow occurs after a number of seconds (up to 10) in the horizontal position, and this time is recorded;
(4) Flow occurs after 1 bump;
(5) Fracture occurs after 1 bump; the fracture being indicated by a piece of the gelled crude breaking loose from the major portion of the crude;
(6) Flow occurs after 2 bumps;
(7) Fracture occurs after 2 bumps;
(8) Flow occurs after 3 bumps;
(9) Fracture occurs after 3 bumps;
(10) No movement induced by above treatment.

The results are reported in the following manner:

(A) The number above (1–10) describing the observed behavior is noted.

(B) In the case of Observation No. 3, the seconds which elapse until flow occurs are recorded.

(C) In all cases in which flow occurs, the flow (low viscosity, moderate viscosity, high viscosity) and the character of the fluid (smooth and uniform, lumpy) are noted.

The reported results are interpreted as follows:

When a bottle containing a gelled substance is tilted from the vertical position, a stress field is induced in the substance. The magnitude of the stress field increases to a maximum as the bottle approaches the horizontal position.

Thus an observation of 1 indicates the flow occurs under the slightest stress, i.e., the substance is a liquid. An observation of 2 indicates that some stress is required to initiate flow, but the stress required is less than the stress obtained when the bottle is in the horizontal position.

An observation of 3 means the gel strength is not sufficient to withstand the stress field in the horizontal position. The factor of time is introduced because some samples will flow very slowly (almost indetectably) for a few seconds and then slump and become liquid. Presumably, in some cases, the gel structure fails after some critical strain occurs.

Bumping the bottle subjects the gelled crude to a higher stress level because of the negative acceleration. Flow (Observations 4, 6, and 8) after bumping means that the gel structure has broken down through most of the fluid, although in some cases, the fluid will appear to be a slurry. A fracture (Observations 5, 7 and 9) indicates that the crude gel has broken only along the line of maximum stress, but otherwise the gel remains intact. The shape of the pieces which have been observed to break away is quite uniform. The observation of flow in some cases and fracture in others indicates there are two ways in which the gelled crudes can behave. Thus a sample with a rating of 7 (fracture after 2 bumps) is not necessarily softer, or easier to handle than a sample with a rating of 8 (flow after 3 bumps). Actually such a rating indicates that these two samples behave differently when subjected to a stress greater than the strength of the gel. Finally, a rating of 10 indicates the gel strength of the crude is greater than that applied in the test.

In evaluating the results obtained by the present process, pour points are determined by ASTM Method D-97-47. Additionally, maximum pour points are obtained by heating the sample to 200° F. for 1 hour, allowing to cool to room temperature and then freezing overnight at 0° F. or a temperature below the pour point of the sample, whichever is lower, for at least 12 hours.

Properties of typical crudes and mixtures thereof which may be treated by the present process are given below in Table II.

TABLE II

Identification	Amna	Nafoora	Arabian
API° at 60° F	34.8	34.7	33.5
Pour point, ° F	+80	+80	−10
Maximum pour point, ° F	+75	+85	
Kin. vis. at 100° F., cs	17.66	25.0	7.05
Wax content, wt. percent	14.2	15.5	2.0
Yield stress at 32° F., dynes/cm.^{2}	800	800	Pass

The invention is further illustrated by the following examples:

Example I

Amna crude (2.0 gal.) was heated to 200° F. (±5° F.) for 1 hour with stirring in a 5.0 gal. glass reactor. At this temperature, 3.1 g. Elvax 250 dissolved in 10 ml. toluene was introduced. This is equivalent to 0.05 weight percent Elvax 250 in the charge. When the oil temperature dropped to about 180–190° F., the charge was poured into a 5.0 gal. can and brought into the cold-room which was set at centrifuge run temperature. Temperature loss

during this transfer ranged from 5–10° F. Oil cooling rates were obtained by introducing a thermometer into the oil in the can and reading off temperature. In one run (Run 7, of Table III) 2 gal. of oil was introduced to a flask equipped with a condenser and a stirrer and stirred overnight with periodic temperature readings; the cooling rates ranging from 0.5° F. to 2° F./min. The oil charge was allowed to equilibrate overnight under run temperature conditions.

A portion of the equilibrated oil, 2132 g., was charged to the centrifuge burette, and fed into the centrifuge at rates ranging from 325 ml. of 375 ml./5 min. until the entire burette was discharged. The dewaxed oil discharged at rates ranging from 210 g. to 290 g./5 min. (250 ml. to 350 ml./5 min.). At the end of the run, the centrifuge was spun until no additional oil discharged (5 min.). The exit and entrance lines were filled with oil which could not be drained. The centrifuge bowl which was removed at the end of the run contained solid deposits. Next the bowl and its deposits were weighed and the weight subtracted from the tare weight of the bowl to yield the weight of solids. The recovery of dewaxed oil was 1700 g. with 215 g. of solids, while the holdup in the lines was estimated at 250 g. Out of 2132 g. oil charged, 2165 g. was accounted for which indicates 100+ percent recovery.

Example II

A composite wax fraction (140.0 g.) was introduced into a 300 cc. autoclave and blanketed with hydrogen. The wax was treated at 800° F. for 14 hours during which time pressure built up to 140 p.s.i.g. The cracked wax was recovered as a viscous semi-solid which had pour point of +120° F., as against a melting point of +140° F. for the charge. Recovery weight was 140 g. or 100 percent.

Other runs were made following the procedure of Example I. Table III below tabulates the effect of dewaxing upon the gel strength of dewaxed crudes.

TABLE III.—EFFECT OF DEWAXING UPON GEL STRENGTH OF DEWAXED CRUDES[1]

	Crude (or blend)							
	Amna		Amna 80%–Arabian 20%				Nafoora 80%–Arabian 20%	
Run	A[2]	B	C	D[2]	E	F[3]	G[2]	H
Centrifuge temp., ° F		40			40	40		40
Solids, wt. percent		9.3			9.3	14.2		8.4
Elvax 250 (blended into dewaxed oil)	0.05	0.05	0	0.05	0.05	0	0.05	0.05
Oil Tests on 1 Week Storage Samples								
Pour point, ° F	+45	+25	+60	+20	+5	+10	+45	+20
Gel strength	3	1	10	1	1	1	10	1
Oil Tests on 1 Month Storage Samples								
Pour point, ° F				+20	+5			
Gel strength				10	1			

[1] Gel Strength Test: 1 to 3 is a pass.
[2] Data on virgin blends plus 0.05 wt. percent Elvax 250.
[3] Blend of Amna (80%)-Arabian (20%) without additive.

Several interesting conclusions can be drawn from the above Table III.

In particular it should be noted that dewaxed Amna crude (with 9.3 percent of its solids removed) containing 0.05 percent Elvax 250 shows improved pour point and gel strength properties with respect to the base blend. An Amna (80%)-Arabian (20%) blend can be dewaxed (with 14.2 percent of its solids removed) so that it passes TAL specifications without additive or dewaxed (with 9.2 percent of its solids removed) so that it passes with the addition of 0.05 weight percent Elvax 250; the latter is storage stable for over a month while a virgin Amna-Arabian blend containing 0.05 weight percent Elvax 250 is not. Also noteworthy is the observation that dewaxed Nafoora (80%)-Arabian blends (with 8.4 percent of its solids removed) containing 0.05 weight percent Elvax 250 pass TAL specifications while the virgin blend containing the same amount of additive fails.

Substantially similar results are obtained when acrylates, polymethacrylates, ethylene-maleic anhydride copolymers and diesters of such polymers are used in the place of the "Elvax" copolymers. Accordingly, it will be manifest to those skilled in the art that such substitution may be made without departing from the spirit and the scope of the underlying inventive concept and that the same is not limited to the particular examples herein given and described.

What is claimed is:

1. A process for improving the flow characteristics and the gel strength of waxy crudes which comprises preheating such crudes to a temperature ranging from about 160° F. to about 200° F., cooling to a temperature ranging from about 40 to about 60° F., centrifuging to remove at least 50% of wax and recovering dewaxed oil, said crudes being centrifuged in the presence of about 0.005 to 0.05 percent by weight of an ethylene-vinyl fatty acid ester copolymer having a molecular weight of about 20,000 to about 31,000 with a vinyl fatty acid ester content of about 24 to about 34 and a melt index of from 5 to 465 added before cooling.

2. Process according to claim 1, wherein said wax is thermally cracked after removal from said crudes.

3. Process according to claim 1, wherein there is added to said dewaxed oil from 0.005 to 0.05 percent of an ethylene-vinyl fatty acid ester copolymer having a molecular weight of about 23,000 to about 27,000 with a vinyl fatty acid ester content of about 27 to 29 and a melt index of from 12 to 18.

4. A process according to claim 1, wherein said centrifuging is carried out with a force of between about 8,000 and 15,000 g's.

5. A proces according to claim 1, wherein said centrifuging is carried out for a residence time of about 10 to about 60 seconds.

6. A process according to claim 2 wherein the fluid produced by cracking said wax is added to the dewaxed oil.

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HERBERT LEVINE, Primary Examiner

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