United States Patent Office 3,679,582 Patented July 25, 1972

3,679,582

FLOW IMPROVEMENT OF WAXY HYDROCARBON WITH THE AID OF POLYSACCHARIDE DERIVATIVES

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No Drawing. Filed Oct. 8, 1969, Ser. No. 864,900
Int. Cl. C09k 3/00
U.S. Cl. 252—8.3 12 Claims

ABSTRACT OF THE DISCLOSURE

A method of transporting waxy liquid hydrocarbons through conduits without causing waxy deposition or plugging of the conduits and improving the flow characteristics of the hydrocarbon by addition to said hydrocarbons a small amount of a polysaccharide derivative having saturated aliphatic hydrocarbon chains of at least 15 carbon atoms in the molecule.

This invention relates to improvement of flow characteristics of waxy liquid hydrocarbons such as waxy crude oil and fractions thereof such as waxy heavy fuels through conduits such as well tubing, pipelines and the like, said flow characteristics being related to improved friction and pour point reduction as well as viscosity and yield stress improvement of said hydrocarbons by incorporating therein a small, but effective amount, of a polysaccharide derivative having at least one saturated aliphatic hydrocarbon chain of at least 15 carbon atoms in the molecule.

BACKGROUND OF THE INVENTION

When waxy oils are cooled to below a particular temperature, the wax present therein gradually separates off. As the separated wax crystals build up into a three-dimensional structure the oil takes on a certain stiffness. At a sufficiently low temperature the oil may even solidify completely. The presence of crystallized wax in oil has an unfavorable influence on the flow properties and, hence, on the handleability of the oil. The difficulties to which the crystallization of wax in crude oils and heavy fuels may lead will be further explained below.

In the production of waxy crude oil by means of a drilled well which passes through formations where lower temperatures prevail than in the formation producing the crude oil, the oil that comes into contact with the cold hole wall may stiffen, whereby the transport of the crude oil to the surface is hampered. If the production is interrupted, it may even happen that all of the crude oil stiffens, which presents serious problems when the production is resumed.

When waxy crude oils and heavy fuels are stored in tanks which are not heated or insulated, the oil which is in contact with the cold walls of the tank will cool down, and so may stiffen. This leads to difficulties when the oil is pumped from the tanks. Especially in the storage of crude oil considerable amounts of stiffened oil may remain in the tanks, which reduces the effective capacity of the tanks.

This problem is even more important in the transport of waxy crude oil in unheated tankers, where the walls of the compartments are partially formed by the ship's wall, which is in direct contact with the cold sea water. That large amounts of stiffened oil remain in the tanks after discharging means that the ship's effective carrying capacity is reduced and also that there is a risk of contamination of subsequent cargoes of crude oil.

The reduced liquidity of waxy crude oils and heavy fuels at a relatively low temperature will also considerably hamper the transport of these oils through a pipeline.

During the pumping of waxy crude oils and heavy fuels through a pipeline high flow resistances may occur, which necessitate a very high pump power. This may give rise to high transport costs especially in the case of trunk pipelines. If the resistance is very high, the available pump pressure or the maximum admissible pressure determined by the strength of the pipe may be insufficient, so that pumping of the oil is impossible.

If pumping is interrupted while the oil is present in the pipeline, the oil, which is often warmer than the environment, will cool down. The wax that is liberated upon cooling may freely build up into a three-dimensional structure, which may extend over the entire cross-section of the pipeline and requires a very high pressure to be broken down. If this pressure exceeds in the available or admissible pressure, the transport can no longer be resumed.

When waxy crude oils and heavy fuels are pumped through a pipeline, as well as when they are stagnant therein, the oil may harden on the cold pipe wall into a layer that remains behind. As a result, the capacity of the pipeline is reduced and there is a risk of contamination of subsequent batches of oil that are to be pumped through the pipeline.

In certain treatments in the refining of crude oil, such as the separation of water, or sediment, it is desirable that the oil should be thin-liquid. If the oil, owing to the crystallized wax present therein, exhibits insufficient flow, then there is the risk that these treatments cannot be carried out to a sufficient extent and sometimes cannot be carried out at all.

The field of application of waxy heavy fuels is a very wide one, the fuel having to meet special requirements according to the specific use. These requirements have been laid down in a number of specifications, the most important of which are concerned with the flow properties. The waxy heavy fuels are used, inter alia, as fuel oils for heating purposes and as fuels for slow diesel engines.

As appears from the foregoing, the flow properties are an important factor in the production, storage, transport and processing of crude oil as well as in the storage, transport and use of heavy fuels. It is, therefore, of paramount importance that the unfavorable influence of wax on the flow properties of these products should be reduced as much as possible.

In order to predict the flow behavior of a waxy crude oil or heavy fuel under operating conditions, a number of laboratory-scale measurements are carried out to determine quantities that are considered characteristic of the flow behavior of the oil, viz the pour point, the viscosity and the yield stress.

The pour point is considered the criterion of the lowest admissible temperature for storage, transport or use, or during a possible interruption of the transport.

The yield stress gives an idea of the shearing stresses that can be expected if a stagnant oil is to be set in motion.

The viscosity is especially connected with the resistance to which the oil is subject during the pumping.

In general, it may be stated that as a waxy crude oil or heavy fuel has a lower pour point, a lower yield stress and a lower viscosity, this oil will have a better handleability in actual practice.

In the past various compounds were proposed, which were claimed to be capable, upon being added to a waxy oil, of improving the flow properties thereof. Although favorable results were obtained by the use of a number of these compounds in lubricants and in some gas oils, in the

majority of cases they proved to be inactive in waxy crude oils and heavy fuels.

SUMMARY OF THE INVENTION

It has now been found that the properties of crude oils and heavy fuels, more particularly the flow properties of waxy crude oil and waxy heavy fuels, can be improved in a simple manner by the incorporation into the oil of a small amount of certain polysaccharide derivatives. For it has been found that polysaccharide derivatives having saturated aliphatic hydrocarbon side chains with more than 15 carbon atoms are, even in low concentrations, capable of improving the properties of crude oils and heavy fuels, more particularly of considerably reducing the pour point, the yield stress and the viscosity of waxy crude oils and heavy fuels.

The following may serve to illustrate that the above actually constitutes a very specific invention, both with respect to the compounds chosen and with respect to the oils and properties of which they can improve.

When the present polysaccharide derivatives were used in waxy lubricating oils, no improvement of the flow properties was observed. Related polyalcohol derivatives, having just as the present compounds saturated aliphatic hydrocarbon side chains with more than 15 carbon atoms, but derived from polyalcohols pertaining to a different class from that to which the polysaccharides pertain, were found incapable of improving the flow properties of waxy crude oils and heavy fuels.

Thus, the invention relates to a process for the preparation of crude oils and heavy fuels having improved properties by incorporation into a crude oil or heavy fuel of polysaccharide derivatives having saturated aliphatic hydrocarbon side chains with more than 15 carbon atoms. The invention relates in particular to a process for the preparation by incorporation into the oil of the above-mentioned polysaccharide derivatives.

For shortness, in this patent application saturated aliphatic hydrocarbon side chains with more than 15 carbon atoms will hereafter be referred to as long hydrocarbon side chains.

Concerning the heavy fuels in which the present polysaccharide derivatives can be employed, preference is given to heavy fuels that at least partially consist of residual components or components obtained as flashed distillate in the flashing of an atmospheric-distillation residue (long residue) of a crude oil. As regards the preparation of these heavy fuels the following may be added.

According to their method of preparation fuels are divided into residual fuels and distillate fuels. Residual fuels contain a certain percentage of residual components. The proportion of residual components in these fuels may vary between wide limits, but is in many cases 20 to 80 percent by weight of the total residual fuel. The residual components may have been obtained, inter alia, as residue in the distillation of crude oil either at atmospheric pressure (long residue) or at reduced pressure (short residue.) They may also be residues obtained in thermal or catalytic cracking processes. As the residual products often have too high a viscosity, they are blended with distillate oils, such as gas oils, for the preparation of fuels.

According to their boiling range distillate fuels may be divided roughly into gasolines, kerosines and gas oils. A special class of distillate fuels is formed by what is known as the flashed distillates. The preparation thereof takes place as follows. A crude oil is distilled at atmospheric pressure to a bottom temperature of approximately 350° C. The residue thus obtained (long residue) is subsequently separated into a flashed distillate and a residue (short residue) by flashing at a strongly reduced pressure. In flashing, the pre-heated feed is introduced continuously into a flash chamber, where evaporation takes place under constant conditions of equilibrium. Gaseous and liquid products are removed continuously. Fractionation is of no importance in flashing. The temperature at which flashing is carried out is limited in view of possible cracking and coke formation. These side reactions become important if the temperature rises too far above 400° C. Flashing is carried out at a strongly reduced pressure in order that a high yield of distillate may be obtained from a given residue (long residue). On account of the distillation method used the flashed distillates contain relatively high paraffins which are normally found in residues and crude oils only. Because of the presence of these relatively high paraffins which are generally not present in the usual distillate fuels such as gas oils, the flashed distillates closely resemble residual fuels and crude oils, especially as far as their behavior at relatively low temperatures is concerned.

Depending on the origin of a waxy crude oil and on the mixing ratio and the nature of the components of waxy heavy fuels, the total wax content may vary between wide limits.

The difficulties to which the presence of wax in crude oils and heavy fuels gives rise are more manifest according as the oil contains more wax and the wax has a higher melting point and a higher boiling point. Especially the presence of wax having a melting point above 35° C. and a boiling point above 350° C. has a very unfavorable influence on the flow properties of these oils, in particular if the oils contain more than 3% by weight of this wax. It has been found that the present polysaccharide derivatives are very active especially in waxy crude oils and heavy fuels of this type.

The polysaccharides from which the present compounds are derived consist of molecules built up of more than five monosaccharide units. Preference is given to polysaccharides built up of glucose units. Examples of such polysaccharides which are built up of glucose units and which may be represented by the general formula $(C_6H_{10}O_5)_n$ with $n>5$ are starch-paste, dextrins, starch, amylose, amylopectin and cellulose. As regards the composition of these polysaccharides the following may be added.

Starch-paste is formed on heating starch with water. In this treatment the starch granules strongly swell to form a gel.

Dextrins are intermediate products of the hydrolysis of starch to glucose. They are colloidal substances, whose particle size is smaller than that of the original starch.

Starch consists mainly of two components: amylose and amylopectin. Both are polysaccharides built up of glucose units, but they have different structures. Depending on the type of starch, the proportions of amylose and amylopectin present therein may vary widely. Some types of starch even are known which consist exclusively of amylose or exclusively or amylopectin.

Amylose consists of unbranched chains of glucose units which have a pyranoid structure and are α-glucosidically bonded.

Amylopectin consists of branched chains of glucose units which have a pyranoid structure and are α-glucosidically bonded.

Cellulose consists of unbranched chains of glucose units which have a pyranoid structure and are β-glucosidically bonded.

In order to be suitable for use according to the invention, the polysaccharide derivatives should contain long hydrocarbon side chains. Preference is given to polysaccharide derivatives in which the long hydrocarbon side chains are unbranched, i.e. polysaccharide derivatives in which the long hydrocarbon side chains can be represented by the general formula $CH_3—(CH_2)_n—CH_2$ where $n>14$. Use will preferably be made of polysaccharides in which the number of carbon atoms in the long hydrocarbon side chains is not higher than 30, more particularly at least 17 and not higher than 26. In addition to long hydrocarbon side chains, which should be present in the polysaccharide derivatives according to

the invention, other side chains may be present therein, such as hydrocarbon side chains having fewer than 16 carbon atoms.

The polysaccharide derivatives that can be employed according to the invention consist of one or more main chains built up of monosaccharide units, which main chains carry long hydrocarbon side chains. The long hydrocarbon side chains may be linked to the monosaccharide units either directly or indirectly. In the former case no further atoms are present between the first carbon atom of the long hydrocarbon side chain and the oxygen atom of the monosaccharide units to which the side chain is linked. If the long hydrocarbon side chains are linked to the monosaccharide units indirectly, one or more other atoms such as one or more carbon, oxygen and/or nitrogen atoms are present between the first carbon atom of the long hydrocarbon side chain and the oxygen atom of the monosaccharide unit to which the side chain is linked. Preference is given to polysaccharide derivatives built up of glucose units in which the long hydrocarbon side chains are linked indirectly to an oxygen atom of the glucose units via a carbonyl group. Polysaccharide derivatives in which one or more long hydrocarbon side chains are linked to each monosaccharide unit as well as polysaccharide derivatives in which one or more long hydrocarbon side chains are linked to some of the monosaccharide units, while these long hydrocarbon side chains are absent in other monosaccharide units of the polysaccharide derivative, are suitable to be used according to the invention.

The polysaccharide derivatives in which the long hydrocarbon side chains are linked indirectly to an oxygen atom of the glucose units via a carbonyl group may be prepared, for instance, by reacting the polysaccharide with an aliphatic acid chloride having a saturated hydrocarbon group with more than 15 carbon atoms. Examples of suitable acid chlorides are acid chlorides derived from saturated aliphatic monocarboxylic acids with more than 16 carbon atoms per molecule, such as stearic acid, arachidic acid and behenic acid and mixtures of such acids, such as mixtures of hydrogenated rape oil fatty acids.

The molecular weight of the polysaccharide derivatives according to the invention may vary between wide limits. By preference, polysaccharide derivatives will be chosen of which the average molecular weight (number average molecular weight M_n) is between 1,000 and 1,000,000, more particularly between 4,000 and 100,000.

Depending on the composition of the crude oils and heavy fuels, it may be preferable to incorporate therein polysaccharide derivatives according to the invention in which the long hydrocarbon side chains do not all have the same number of carbon atoms.

Although derivatives of polysaccharides containing long hydrocarbon side chains are generally suitable to the improvement of the properties of crude oils and heavy fuels, a special interest is taken in the following polysaccharide esters: amylose stearate, dextrin stearate, esters of amylose and hydrogenated rape oil fatty acids and esters of dextrin and hydrogenated rape oil fatty acids.

The concentration in which the polysaccharide derivatives may be employed may vary between wide limits, depending on the nature, the structure and the molecular weight of the polysaccharide derivative to be used, the composition of the crude oil or heavy fuel and the envisaged improvement of the properties. In some cases an amount as low as 0.001% by weight calculated on the oil is sufficient to produce the desired effect. In the majority of cases an amount of 2.0% by weight is amply sufficient. By preference, 0.002 to 0.2% by weight of the polysaccharide derivatives is incorporated into the oil.

As the present compounds have the properties, inter alia, of reducing the pour point, the viscosity and the yield stress of waxy crude oil and heavy fuels, they may, in view of each of these individual properties be referred to, if desired, as pour point reducers, viscosity reducers, or yield-stress reducers instead of as flow improvers. In this respect it should be added that in general a compound may be considered to belong to the class of the pour-point reducers only if it is capable of reducing the pour point by at least 6° C., while it is used in a concentration not exceeding 0.2% by weight.

A special object of the use of the present additives in waxy crude oils is to prevent difficulties which the wax present in the crude oil may cause at low temperatures in the storage as well as in the transport of the oil through pipelines, with tankers or in some other way. The compounds are also very suitable to be used in oil wells producing waxy crude oil, to prevent the formation of waxy deposits or to dissolve deposits present on the walls of the well. A special object of the use of the present compounds as additives to waxy heavy fuels is to prevent difficulties which the wax present in the heavy fuel may cause at low temperatures in storage and transport as well as in uses where the fuel often has to pass through filters and narrow openings.

If the present polysaccharide derivatives are used as additives which are to improve the properties of heavy fuels, the fuels may in addition contain small amounts of other compounds which are in general usually added to fuels of this type. Examples of such compounds are antioxidants anticorrosive additives, metal deactivators and additives to prevent the clogging up of filters and the formation of an emulsion.

PREFERRED EMBODIMENT OF THE INVENTION

The invention will now be further elucidated by means of the following examples.

(1) Esters of amylose and stearic acid

Stearoyl chloride was added in an amount of 98 g. to 10 g. of amylose in 100 g. of dry pyridine, and the mixture was kept at 100–120° C. for 24 hours. After addition of toluene, the mixture was filtered and the filtrate poured into methanol. The polysaccharide derivative thus precipitated was taken up in toluene for further purification and precipitated once more by pouring the solution into methanol. After drying, the yield of esters of amylose and stearic acid was 56 g. $\overline{M}_n$=69,000.

(2) Esters of dextrin and stearic acid

The preparation was effected in the same way as described under (1), except that it started from 10 g. of dextrin.

The yield was 60 g. of esters of dextrin and stearic acid, with $\overline{M}_n$=31,000.

(3) Esters of amylose and hydrogenated rape oil fatty acids

Acid chloride of hydrogenated rape oil fatty acids was added in an amount of 33 g. to 3 g. of amylose in 50 g. of dry pyridine, and the mixture was boiled under reflux for 12 hours. (The hydrogenated rape oil fatty acids from which the acid chlorides used were derived had the following composition: 1.7% C_{16}; 44.2% C_{18}; 7.3% C_{20}; 46.1% C_{22}; 0.7% C_{24}.) After addition of toluene the mixture was filtered and the filtrate poured into ethanol. The polysaccharide derivative thus precipitated was filtered off and washed with ethanol. After drying, the yield of esters of amylose and hydrogenated rape oil fatty acids was 21 g. $\overline{M}_n$=19,800.

(4) Esters of dextrin and hydrogenated rape oil fatty acids

The preparation was effected in the same way as described under (3) except that it started from 3 g. of dextrin.

The yield was 25 g. of esters of dextrin and hydrogenerated rape oil fatty acids, with $\overline{M}_n$=20,100.

In order also to ascertain the behavior of related compounds, the following compounds were prepared (5–7):

(5) Hexaester of dipentaerythritol and stearic acid.

(6) Hexaester of dipentaerythritol and hydrogenated rape oil fatty acids.

(7) Tetraester of pentaerythritol and behenic acid.

The above-mentioned compounds 1–7 were tried as flow improvers in one or more of the following waxy oils.

Oil I.—Residual fuel having a pour point determined by method B of 32° C., a kinematic viscosity of 35 cs. at 50° C., and a wax content of 10% by weight, composed of 49% by weight of a residue obtained in the atmospheric distillation of a crude oil from West Africa and 51% by weight of a hydrocarbon oil distillate.

Oil II.— Residual fuel having a pour point determined by method B of 26° C., a kinematic viscosity of 14 cs. at 50° C. and a wax content of 10.5% by weight, composed of 60% by weight of a residue obtained in the atmospheric distillation of a crude oil from North Africa and 40% by weight hydrocarbon oil distillate.

Oil III.—Distillate fuel having a pour point determined by method A of 38° C., a kinematic viscosity of 25 cs. at 50° C., and a wax content of 13% by weight, obtained as flashed distillate in the flashing of an atmospheric residue of a crude oil from North Africa.

Oil IV.—Crude oil from North Africa having kinematic viscosity of 3.66 cs. at 37.8° C., a wax content of 7.8% by weight, a pour point determined by method A of 5° C. and a pour-point determined by method C of 2° C.

Oil V.—Crude oil from West Africa having a kinematic viscosity of 2.70 cs. at 50° C., a wax content of 7.0% by weight, a pour point determined by method A of 14° C. and a pour point determined by method C of 11° C.

Oil VI.—Lubricating oil having a kinematic viscosity of 5.5 cs. at 100° C. and a pour point determined by method A of −9.5° C., prepared from a crude oil from the Middle East.

More than 75% by weight of the wax present in heavy fuels I, II and III was wax having a melting point above 35° C. and a boiling point above 350° C. More than 50% by weight of the wax present in crude oils IV and V was wax having a melting point above 35° C. and a boiling point above 350° C.

Pour point.—The influence of compounds 1–7 on the pour point of heavy fuels, crude oils and lubricating oil is represented in the table. The values given therein indicate the reduction, in degrees centigrade, of the pour point of the oil upon these compounds being incorporated into the oil.

As regards the methods of determining the pour point of waxy crude oils the following should be added.

The pour point of a waxy crude oil is often dependent on the preliminary thermal treatment to which the oil has been subjected. On the basis of whether or not a preliminary thermal treatment has been carried out, the methods suitable for the determination of the pour point of waxy crude oils may be divided into two groups.

(1) Methods by which the pour point is determined on a sample which has not been re-heated before the determination (for instance, method C).

(2) Methods by which the sample is heated to 46° C. just before the determination (for instance method A).

The thermal treatment gives, in certain cases, a higher pour point, but seems less realistic, since the crude oil concerned does not undergo such a temperature cycle in actual practice.

The table shows that the polysaccharide derivatives according to the invention are capable of reducing the pour point in general sense, i.e. independent of a preliminary thermal treatment is given.

The pour-point test methods A, B, and C mentioned in the table are carried out as follows.

Method A.—The two samples of the oil are heated to 65° C., and at this temperature the additive is added to one of the samples. After cooling to room temperature, the pour point is determined as described for the ASTM maximum pour point in ASTM D97–66.

Method B.—Two samples of the oil, of which one contains the additive, are heated, with stirring, to 104° C., and then rapidly cooled to −20° C. Subsequently, the samples are heated to 46° C. Then, for the determination of the pour point, the ASTM standard method D97–66 is followed from the point where it specifies cooling from 46° C.

Method C.—Two samples of the oil are heated to 65° C,. and at this temperature the additive is added to one of the samples. The samples are then cooled to room temperature. Then, for the determination of the pour point, the ASTM standard method D97–66 is followed from the point where, during cooling from 46° C., room temperature is passed.

Yield stress.—A sample of waxy hydrocarbon oil is heated to 65° C., and at this temperature the desired amount of polysaccharide derivative is added to the sample. After cooling to room temperature, a steel U-tube of 54 cm. length and 3.8 mm. internal diameter is filled with the oil to be tested. Subsequently, the oil in the tube is cooled to the test temperature, after which the pressure on one of the legs of the U-tube is gradually raised. The pressure (P_o) at which the first flow is observed is used for calculating the yield stress.

The yield stress (defined as the shearing stress required for setting a solidified oil in motion) is calculated from the observed P_o with the aid of the formula:

$$\tau_o = \frac{P_o \cdot D}{4L}$$

		Type of oil														
		Heavy fuel							Crude oil						Lubricating oil	
		Number of the oil														
		I		II		III			IV				V		IV	
		Pour point determined by method—														
		B				A			C		A		C		A	
		Concentration of the additive, percent														
	Additive	0.08	0.02	0.08	0.02	0.08	0.02	0.01	0.025	0.01	0.025	0.01	0.01	0.01	0.1	0.05
No.	Composition	Reduction of the pour point, ° C.														
1	Esters of amylose and stearic acid		18												0	0
2	Esters of dextrin and stearic acid		18													
3	Esters of amylose and hydrogenated rape oil fatty acids.		18	18		24	21	18		15	15	9	9	12	0	0
4	Esters of dextrin and hydrogenated rape oil fatty acids.		27	15		27	15	12	15	12	12	9	24	27		
5	Hexaester of dipentaerythritol and behenic acid	0	0	0	0											
6	Hexaester of dipentaerythritol and hydrogenated rape oil fatty acids.	0	0	0	0											
7	Tetraester of pentaerythritol and behenic acid	0	0	0	0											

where

τ_o=yield stress, dynes/cm.^{2},
P_o=pressure at which the first flow is observed, dynes/cm.^{2},
D=diameter of the tube, cm.,
L=length of the tube, cm.

The yield stress of a sample of crude oil (oil V) to which 0.005% by weight of esters of dextrin and hydrogenated rape oil fatty acids (compound 4) had been added was determined in the above-described way at two temperatures and compared with the yield stress of a sample of the same crude oil which did not contain an additive but had been subjected to the same preliminary thermal treatment. The results are given below.

Oil V:
Yield stress at 8° C: 302 dynes/cm.^{2}
Oil V+0.005% by weight of compound 4:
Yield stress at 8° C: 15 dynes/cm.^{2}
Yield stress at 0° C: 80 dynes/cm.^{2}

Viscosity.—Since at lower temperatures waxy hydrocarbon oil behaves as non-Newtionian liquids, the viscosity of such oils can be determined in a realistic manner only in a viscometer in which ether the shearing stress or the rate of shear can be adjusted and kept constant within narrow limits. The Ferranti Portable Viscosimeter Model VL, a so-called Couette coaxial-cylindrical viscometer of the constant-shear-rate type, is very suitable for determining viscosities of waxy hydrocarbon oils.

A sample of waxy hydrocarbon oil is heated to 65° C., and at this temperature the desired amount of polysaccharide derivative is added to the sample. After cooling to room temperature, the reservoir of the viscometer is filled with the oil to be tested.

The viscosity of a sample of crude oil (oil V) to which 0.005% by weight of esters of dextrin and hydrogenated rape oil fatty acids (compound 4) had been added was determined in the above-described manner and compared with the viscosity of a sample of the same crude oil which did not contain an additive but had been subjected to the same preliminary thermal treament. The results are given below:

Oil V: Equilibrium viscosity at 5° C. and rate of shear 318 s.$^{-1}$=30 cp. (reached after 60 minutes).
Oil V+0.005% by weight of compound 4: Equilibrium viscosity at 5° C. and rate of shear 318 s.$^{-1}$=12 cp. (reached after 5 minutes).

We claim as our invention:

1. A method for improving flow characteristics of waxy liquid hydrocarbons selected from the group consisting of waxy crude oil and waxy heavy fuels through conduits by incorporating into the waxy hydrocarbons a small amount of a polysaccharide ester of a saturated fatty acid having at least 15 carbon atoms, said polysaccharide portion of said ester containing more than five glucose units and thereby preventing waxy deposition on conduit walls during transportation of the hydrocarbons.

2. The method of claim 1 wherein the polysaccharide ester consists of an ester of amylose and stearic acid.

3. The method of claim 1 wherein the polysaccharide ester consists of an ester of dextrin and stearic acid.

4. A method for improving the flow characteristics of waxy crude oil through a pipeline line comprising injecting into a pipeline through which waxy crude oil flows a small amount of a saturated fatty acid ester of a polysaccharide of more than five glucose units said saturated fatty acid having at least 15 carbon atoms in the molecule and flowing the oil through the line.

5. The method of claim 1 wherein the molecular weight of the polysaccharide ester is between about 1,000 and about 1,000,000 and is present in an amount of from about 0.001% to about 2% by weight.

6. The method of claim 5 wherein the polysaccharide ester consists of an ester of amylose and stearic acid.

7. The method of claim 5 wherein the polysaccharide ester consists of an ester of dextrin and stearic acid.

8. The method of claim 5 wherein the waxy crude oil contains at least 3% of wax having a melting point above 35% C. and a boiling point above 350° F.

9. The method of claim 1 wherein the polysaccharide ester consists of an ester of amylose and hydrogenated rape oil fatty acid.

10. The method of claim 1 wherein the polysaccharide ester consists of an ester of dextrin and hydrogenated rape oil fatty acid.

11. A method for improving flow characteristics of waxy liquid hydrocarbons selected from the group consisting of waxy crude oil and waxy heavy fuels through conduits by incorporating into the waxy hydrocarbons a small amount of amylose stearate and thereby preventing waxy deposition on conduit walls during transportation of the hydrocarbons.

12. A method for improving flow characteristics of waxy liquid hydrocarbons selected from the group consisting of waxy crude oil and waxy heavy fuels through conduits by incorporating into the waxy hydrocarbons a small amount of dextrin stearate and thereby preventing waxy deposition on conduit walls during transportation of the hydrocarbons.

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U.S. Cl. X.R.

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