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FILTER AID FOR DEWAXING MINERAL OILS
John L. Tiedje and Stephan Ilnyckyj, Sarnia, Ontario,
Canada, assignors to Esso Research and Engineering
Company, a corporation of Delaware
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The present invention relates to an improved process for the dewaxing of mineral oils and to the use of an additive which improves the rate of filtration of wax from mineral oil. This invention particularly relates to the use of an additive which improves the rate of filtration of the waxy constituents from petroleum middle distillates and lube oil fractions. Specifically, this invention concerns the use of an ethylene-vinyl acetate copolymer as a filtering aid.

Dewaxing is one of the more important processes used in the preparation of petroleum lubricating oils since removal of the wax results in an oil of markedly improved cloud and pour points. The process is usually carried out by chilling the oil in order to precipitate the wax, followed by filtering of the wax from the oil. It is common practice to add solvents to the oil which tend to dissolve the oil and precipitate the wax. Solvents which may be used are liquid paraffins of low boiling point, such as propane, butane, pentane, hexane and light petroleum oils, mixtures of ketones and aromatic hydrocarbons, such as methyl ethyl ketone, benzene or toluene, and chlorinated hydrocarbons, such as dichloro ethane and trichloro ethane. In the commercial processes for removing wax from lubricating oil stocks, propane, propane/butane, MEK/toluene and methyl ethyl ketone (MEK)/methyl isobutyl ketone (MIBK) dewaxing solvents are used. After the waxy constituents of the mineral oils are precipitated, during the subsequent filtration step there is a tendency for wax crystals to block the filters. This markedly increases the time of filtration and also the amount of oil trapped in the wax cake.

An ever-increasing demand for low cloud and pour petroleum middle distillate products, such as diesel fuels, jet fuels, etc., makes their dewaxing a very desirable operation. However, very low filter rates are obtained when dewaxing such middle distillates in the absence of a solvent due to the tendency of wax crystals to restrict the flow of filtrate. The yield of dewaxed oil is also very low, because of liquid hold-up in the voluminous filter cakes that are formed. Although the addition of a solvent would somewhat improve the filtration, the high cost of refrigerating and recovering the solvent makes the operation uneconomical. For these reasons, the dewaxing of middle distillates has never been put into practice on a large scale.

Applicants have now unexpectedly found that adding small amounts of ethylene-vinyl acetate copolymer to the mineral oil to be dewaxed improves the filter rate, the yield of dewaxed oil, and produces a drier filter cake. There are several materials known to applicants which have been used as pour depressants for petroleum oils. The following materials, namely, Paraflow (an alkylated naphthalene), Acryloid 150 (a polymer of lauryl methacrylate), and applicants' ethylene-vinyl acetate copolymer are known to applicants as pour depressants, the first two for lubricating oils and the last for middle distillates.

Applicants' ethylene-vinyl acetate copolymer when used in concentrations of 0.1 wt. percent only lowers the pour point of SAE 5 oil by about 5° F., from -20 to -25° F. The pour point of SAE 10 or more viscous oils of paraf-

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finic type (e.g., those obtained from Leduc crude by distillation, dewaxing phenol extraction and clay treatment) was not affected by addition of ethylene-vinyl acetate copolymer. Obviously, the copolymer is ineffective in lowering the pour point of lubricating oils. In contrast, however, 0.05 wt. percent of the copolymer lowered the pour point of a middle distillate oil, namely, Sarnia heating oil (a 50/50 blend of virgin and cracked gas oils boiling between 410° and 660° F.), from +25° F. to about -70° F.

In Table I, below, the pour depressant activity on this heating oil of Paraflow, Acryloid, and applicants' copolymer is compared.

Table I.—Effect of various additives on ASTM pour points of a 410° to 660° heating oil ¹

Additive	Wt. percent	ASTM Pour, ° F.
None		+25
“Paraflow”	0.5	+20
	1.0	+10
	1.5	+5
“Acryloid”	0.2	+20
	0.5	+20
	1.0	+15
Ethylene Vinyl Acetate Copolymer (Mol. Wt. 1750). ²	0.05	-40
	.1	<-70
	.25	<-70
	.5	-40

¹ 50/50 blend of virgin and cracked gas oils.
² As determined by Rast method.

It is apparent from the above table that Paraflow and Acryloid are relatively ineffective in lowering the pour point of the heating oil, whereas the copolymer is an excellent pour depressant.

On the other hand, the copolymers have proven to be ineffective as pour depressants for lubricating oils as shown below in Table II.

Table II

Weight Percent Copolymer (Mol. Wt. 800)	ASTM Pour, ° F.		
	MCT-10 ¹	MCT-30 ¹	MCT-60 ¹
None	+5	+30	+35
0.1	+15	+30	+45
0.5	+15	+25	+40

¹ Paraffinic type obtained from Leduc crude by distillation, dewaxing, phenol extraction and clay treatment.

The pour depressants used have little effect on oil viscosity, particularly in the concentration ranges in which they are effective. It is probable that the different effects of these materials on the pour point of oils is due at least in part to the structural differences between the waxes present in middle distillate oils (n-paraffins), and dewaxed lubricating oils (isoparaffins and naphthenes).

The principal object of this invention is to set forth an improved process of dewaxing mineral oils by increasing the filter rate and dewaxed oil yields. Another object of this invention is to provide a drier filter cake which is easier to work. A further object is to produce a wax containing applicants' dewaxing aid which can subsequently be hydrofined without contaminating the hydrofining catalyst. Now, in accordance with applicants' invention, wax precipitated from petroleum hydrocarbon oils boiling between 250° F. and 1000° F. can be filtered at a substantially faster rate by incorporating into the petroleum oil, prior to precipitation of the wax, small amounts of an

ethylene-vinyl acetate copolymer. The petroleum oils containing waxy constituents are cooled to precipitate the waxy materials in the presence of minor amounts of ethylene-vinyl acetate copolymer and then filtered. The dewaxing step is carried out at a temperature sufficient to precipitate the desired amount of wax which results in a dewaxed oil of the desired pour point. Filtration may be carried out by applying pressure to the feed side of the filter, or suction to the product side of the filter. The method used will depend upon the materials being dewaxed and which solvent, if any, is used. The pressure at which the wax is filtered is not critical.

Applicants' filtering aid improves the economy of dewaxing by increasing the filtration rate, increasing the yield of dewaxed oil, savings made on solvent, its chilling and recovery. The use of applicants' filtering aid can reduce the size of a dewaxing plant for comparable capacity and lower the cost of operation. A further advantage is that waxes obtained in accordance with applicants' process may be hydrofined without contaminating the hydrofining catalyst.

The pour point depressant comprises ethylene-vinyl acetate copolymer. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 60 to 99% as compared to parts by weight of vinyl acetate in the range from about 40 to about 1%. A desirable ethylene-vinyl acetate copolymer contains about 15 to 25% by weight of vinyl acetate, as for example, about 20% parts by weight of vinyl acetate. The molecular weight of the ethylene-vinyl acetate copolymer should be in the range from about 800 to 3,000, preferably in the range from about 1,500 to 2,200. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The ethylene-vinyl acetate copolymer as described above is used in a concentration in the range from about .001 to .5 wt. percent of oil treated, preferably in a concentration in the range from about .005 to .2 wt. percent and more preferably at about .05 wt. percent.

These low molecular weight copolymers have no effect upon the pour points of lubricating oils, thus emphasizing the difference in structure between the wax associated on the one hand with lube oils and on the other with middle distillates. The low molecular weight copolymers may be prepared by a peroxide process. In some instances, it may be desirable to first prepare a higher average molecular weight polymerization product and then recover from that product material having a molecular weight within the range between about 800 and about 3,000. Since such polymerization products normally consist of a mixture of polymers whose molecular weights vary over a wide range, an effective method for recovering the 800 to 3,000 molecular weight portion therefrom is to extract the product with a solvent such as normal heptane or methyl-ethyl ketone. One method of making the copolymers is to conduct the polymerization in a benzene solution using di-tertiary-butyl-peroxide as an initiator at a temperature in the range from about 280° to 340° F. The preferred temperature is about 300° F. The pressure is in the range from about 700 to 2,000 p.s.i.g., preferably at about 800 p.s.i.g. The autoclave or similar equipment containing the solvent, initiator and vinyl acetate is purged about three times with nitrogen, twice with ethylene and then charged with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the polymerization, additional ethylene is added whenever the pressure drops by about 100 p.s.i.g. Polymerization is considered complete when it is less than 50 p.s.i.g. pressure drop per hour. The product is stripped free of solvent and unreacted vinyl acetate under vacuum.

Applicants' filter aid may be used in the conventional propane/butane, MEK/toluene, and MEK/MIBK dewaxing processes. These processes are all used commercially and would only require adding applicants' filtering aid

prior to precipitating the wax from the oil which is to be dewaxed. Applicants' filtering aid can also be used in dewaxing middle distillate oils which are dewaxed under conditions in which a solvent may or may not be present. Prior to the filtration step, various solvents may be added to reduce the viscosity and aid in the filtration, e.g., low boiling liquid paraffins, light petroleum oils, ketones, aromatic compounds such as propane, benzene, toluene and acetone, and higher ketones and mixtures thereof.

The dewaxing may be carried out in a conventional manner after adding applicants' copolymer by cooling the petroleum oil containing the waxy constituents at a controlled rate and filtering the wax at the dewaxing temperature to obtain the desired pour point of the dewaxed oil. The filtration is generally carried out at temperatures between 32° F. to -60° F. Where MEK/toluene dewaxing process is used, the filtration is carried out at temperatures between +10 and -10° F. Where propane dewaxing is used, the filtration is usually carried out at temperatures between -20 to -40° F. The filtration step is generally carried out at about atmospheric pressure (i.e., ± 5 p.s.i.g.), and in the liquid phase. The pressure at which the wax is filtered is not critical and can vary between +10 and -10 p.s.i.g. depending upon the filtration temperature and the particular solvents used.

The ethylene-vinyl acetate copolymer consists of 1 to 40 wt. percent vinyl acetate and 60 to 99 wt. percent ethylene, preferably 15 to 25 wt. percent vinyl acetate and 85 to 75 wt. percent ethylene. The molecular weight of the copolymer can be 1,000 to 3,000, preferably about 1,500 to 2,200. The concentration of the copolymer added to the petroleum oil to be dewaxed is critical. Concentrations of .005 to 0.25 wt. percent based on the petroleum oil can be used. Though concentrations of .05 to 0.1 wt. percent are preferred, concentrations of .02 to 0.20 can also be used. If too great a concentration of the copolymer is used, the filtering rate is found to be adversely affected.

In accordance with this invention, middle distillate oils boiling between 250° F. and 700° F., and light lubricating oil stocks boiling between 600° F. and 1000° F. and having SAE values of 5 to 20, for example, can be dewaxed and filtered.

To a middle distillate petroleum oil containing waxy constituents is added .02 to 0.2 wt. percent based on petroleum oil, of ethylene-vinyl acetate copolymer consisting of 15 to 25 wt. percent of vinyl acetate and 85 to 75 wt. percent of ethylene based on weight of copolymer and having a molecular weight of 1,500 to 2,200. The petroleum oil is cooled in accordance with conventional practices to precipitate sufficient waxy constituents to obtain the desired pour point of the dewaxed oil and is subsequently filtered to remove the precipitated wax. Where a solvent dewaxing process is utilized, the volume of petroleum oil to solvent can be 1/1 to 1/9. Preferably, the volume of petroleum oil to solvent is 1/1 to 1/4.

Use of applicants' filtering aid has greatly improved the rate at which precipitated wax can be removed from petroleum oils, the yield of dewaxed oil, and the quality of the filter cake.

The invention is further exemplified by various runs reported in the following examples. In several of these examples, comparative runs were made with other known pour depressants to determine their relative effectiveness as filter aids.

EXAMPLE 1

A middle distillate straight run gas oil having a FBP (final boiling point) of 720° F. and an ASTM cloud point of +40° F. and pour point of +40° F. was dewaxed at a temperature of 0° F. and filtered. To the middle distillate was added 0.1 wt. percent of ethylene-vinyl acetate copolymer. The data obtained were com-

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pared with the middle distillate oil not containing the applicants' filtering aid. The results obtained are reported below in Table III.

Table III.—Effect of ethylene-vinyl acetate copolymer¹ on dewaxing of straight run gas oil

Straight run gas oil:	
FBP.....	720° F.
ASTM cloud point.....	+40° F.
ASTM pour point.....	+40° F.
Conditions of dewaxing:	
Solvent.....	None.
Temperature.....	0° F.
Vacuum.....	10" Hg.
Filter leaf.....	0.049 sq. ft.

RATE OF FILTRATION

Filtration Time, secs.	Drying Time, secs.	Filter Aid			
		None		0.1 wt. percent Eth.-V.A. Copolymer	
		Wax, g.	Oil, g.	Wax, g.	Oil, g.
60.....	60	14.5	11.3	8.5	18.35
60.....	60	9.4	11.3	8.0	23.35
60.....	60	10.6	10.3	12.3	22.25
60.....	60	13.1	13.1	13.5	22.5
Average.....		11.9	11.45	10.6	21.6
Dewaxed Oil Yield, wt. Percent.....			49.6		67.2
Dewaxed Oil Filter Rate, U.S.G./sq. ft./hr. ²			1.7		3.3

DEWAXED OIL

	ASTM Cloud Point, ° F.	ASTM Pour Point, ° F.
No Filter Aid.....	+6	+5
0.1 wt. percent V.A.-Eth. Copolymer.....	+8	-55
0.1 wt. percent V.A.-Eth. Copolymer, Dewaxed Oil Redistilled.....	+4	+5

¹ 26.4 wt. percent vinyl acetate, 73.6 wt. percent ethylene, molecular weight 1530.

² Based on a rotary filter turning 2½ minutes/revolution and 40% submerged.

The data in Table III, above, show that the use of applicants' additive doubles the filtration rate (from 1.7 to 3.3 U.S. gallons/square foot/hour) and increases the yield of dewaxed oil by about 35% (from 49.6 to 67.2 wt. percent). Additionally, the amount of copolymer left in the dewaxed oil was sufficient to lower ASTM pour of this dewaxed oil from +5 to -55° F. This additive will also substantially improve the conventional ketone solvent dewaxing processes when used on middle distillates. Solvent dewaxing processes are normally not

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practical for middle distillate fuels. The yield and production capacity of the filter in gallons of dewaxed oil per hour could be further increased by washing the filter cake with a light hydrocarbon solvent which could be subsequently distilled from both dewaxed oil and wax.

The results obtained by using Paraflow and Acryloid 150 as dewaxing aids for middle distillates under comparable conditions are reported in Table IV.

Table IV.—Effect of Paraflow dewaxing aid and Acryloid on dewaxing of straight run gas oil

Straight run gas oil:	
FBP.....	720° F.
ASTM cloud point.....	+40° F.
ASTM pour point.....	+40° F.
Conditions of dewaxing:	
Solvent.....	None.
Temperature.....	0° F.
Filtration time.....	60 secs.
Drying time.....	60 secs.
Vacuum.....	10" Hg.
Filter leaf.....	0.049 sq. ft.

	Paraflow Dewaxing Aid, 0.1 wt. percent		Acryloid 150, 0.1 wt. percent	
	Wax, g.	Oil, g.	Wax, g.	Oil, g.
Rate.....	24.2	9.2	27.5	4.3
Dewaxed Oil Yield, wt. percent.....		27.5		13.5
Dewaxed Oil Filter Rate, U.S.G./sq. ft./hr. ¹		1.4		+0.64

¹ Based on a rotary filter turning 2½ minutes/revolution and 40% submerged.

Comparison of the data presented in Tables III and IV show that applicants' filter aid is unexpectedly superior to either Acryloid or Paraflow as a filter aid for middle distillate oils.

EXAMPLE 2

To an SAE 5 grade lube oil distillate was added ethylene-vinyl acetate copolymer in concentrations of 0.02 to 0.2 wt. percent based on the oil. The oil was cooled to a temperature of 0° F. and filtered. An MEK/MIBK solvent mixture was used and the oil solvent mixture was chilled at a rate of 6° F. per minute. The results obtained using applicants' additive were compared with the results obtained using Paraflow as a dewaxing aid. The comparative data are reported below in Table V and show that when .05 wt. percent ethylene-vinyl acetate copolymer is used, a filtration rate of 2.2 times greater than that obtained with no additive results. It is also noted that the copolymer is substantially better than Acryloid at one-half the concentration and comparable to Paraflow at one-half the concentration. Drier wax cakes were obtained by using the additive and an increase in filter rate of over 100% resulted.

Table V.—Filter rate experiments with dewaxing aids

Conditions: Solvent: 50% MEK 50% MIBK, dilution 1.5 vol. solvent 1 vol. waxy oil. Chill rate 6° F./min., vacuum 10" Hg. Filtering temperature 0° F.
Feedstock: Pffe. 5 distillate (phenol treated, SAE 5 grade oil, boiling range 625 to 880° F., 14.9% wax, visc. 40 SUS at 100° F.)

Feed-Stock	Dilution, v./v.	Dewaxing Aid Additive, Percent of Feed	Filtration Time, secs.	Drying Time, secs.	Liquids: Solids Ratio in Cake, w./w.	Percent Yield Dewaxed Oil	Filter Rate ¹ Waxy Oil, U.S.G./s.f./hr.	Relative Filter Rate	Dewaxed Oil	
									Cloud, ° F.	Pour, ° F.
Pffe. 5 Distillate.....	1.5		60		8.4	36.5	5.3	100	+2, 0	+5
Do.....	1.5	0.02% Copolymer.....	60	60	6.3	41.6				
Do.....	1.5	0.05% Copolymer.....	60	60	8.4	34.3	7.0	132	+4, +4	+10, +5
Do.....	1.5	0.1% Copolymer.....	60	60	6.1	47.7	11.7	221	+2, +4	+5, +10
Do.....	1.5	0.1% Copolymer.....	60	60	7.9	36.5				
Do.....	1.5	0.1% Copolymer.....	60	60	5.8	49.6	9.8	185	+4, +4	+10
Do.....	1.5	0.1% Copolymer.....	60	60	7.6	38.1				
Do.....	1.5	0.1% Copolymer.....	60	60	5.5	51.5	2.6	49	+10	+14
Do.....	1.5	0.1% Paraflow Dewaxing Aid.....	60	60	7.7	38.1	13.3	251	+2, +4	+10, +5
Do.....	1.5	0.1% Acryloid 150.....	60	60	6.2	48.4				
Do.....	1.5	0.1% Acryloid 150.....	60	60	11.1	26.0	7.0	146		
Do.....	1.5	0.1% Acryloid 150.....	60	60	8.9	38.4				

¹ Filter rate calculated in U.S.G. of waxy feed/sq.ft./hr. for a rotary filter, 60 sec. filtering in a 2½ minute revolution.

A further unexpected advantage obtained by using applicants' filtering aid was that the separated waxes could be hydrofined without contaminating the hydrofining catalyst, as other filter aids do.

EXAMPLE 3

A 125° F. melting point recrystallized paraffin wax was hydrofined under conventional hydrofining conditions using a cobalt molybdate catalyst. In one run the recrystallized wax contained no filter aid; in a second run, it contained Paraflow; and in the third run, applicants' ethylene-vinyl acetate copolymer was used. The effect of the presence of the dewaxing aid is demonstrated by the resulting color of the wax product. The data obtained are described in Table VI below.

Table VI.—Comparison of hydrofining of waxes containing copolymer² and Paraflow dewaxing aid

[Hydrofining conditions were the same for all feedstocks]

Feed	Pass No.	Temp., ° F.	Color Saybolt ¹
125° F. MP recrystallized paraffin wax.....	1	500	+35
125° F. MP recrystallized paraffin wax from waxy oil containing 0.15% Paraflow Dewaxing Aid.	1	600	+19
	2	500	+25
125° F. MP paraffin recrystallized from waxy oil containing 0.05% copolymer. ²	1	600	+31
	2	500	+35

¹ Color Saybolt is defined in ASTM D156-53T.

² Ethylene-vinyl acetate copolymer.

From the above examples it is evident that applicants have found a valuable aid for filtering precipitated wax from petroleum oils containing waxy constituents. Applicants have shown that the rate of filtration may be substantially improved, and the yield of dewaxed oil increased. Further, the dewaxing aid does not contaminate the hydrofining catalyst, as Paraflow does, when the precipitated wax is hydrofined.

The present invention is not to be limited by the specific examples, but rather by the scope of the appended claims.

What is claimed is:

1. In the process of solvent dewaxing wherein a lube

oil fraction is solvent dewaxed by diluting with a mixture of 50% MEK and 50% MIBK and chilling at a rate of 6° F./minute to a filtering temperature of 0° F. wherein 0.05 wt. percent of ethylene-vinyl acetate copolymer comprising 26.4 wt. percent of vinyl acetate and 73.6 wt. percent of ethylene based on the wt. of copolymer, having a molecular weight of 1,530 is added prior to filtration, precipitating the wax present in said oil and filtering the precipitated wax.

2. An improved process for dewaxing a lube oil boiling in the range of 600° to 1000° F. which comprises adding from about 0.001 to 0.5 weight percent based on the oil of an ethylene vinyl acetate copolymer comprising 60 to 99% by weight ethylene and from about 1 to 40% by weight of vinyl acetate, said copolymer having a molecular weight in the range from about 800 to about 3000, cooling said oil containing said copolymer to a temperature at which waxy constituents are precipitated therefrom and thereafter filtering the precipitated wax from the said oil.

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DELBERT E. GANTZ, *Primary Examiner.*

ALPHONSO D. SULLIVAN, J. R. LIBERMAN,

Examiners.

H. LEVINE, *Assistan Examiner.*