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PROCESS FOR THE MANUFACTURE OF ASPHALT FROM WAXY MINERAL OILS

Alvin P. Anderson, Berkeley, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to an improvement in the manufacture of asphaltic hydrocarbons from petroleum oils containing both asphalt and wax, by precipitation with normally gaseous hydrocarbons, and more particularly deals with the production of asphalts from these oils by the above method, which asphalts are free from harmful wax.

The precipitation of asphalts from oils containing same by means of normally gaseous hydrocarbons, i. e., those having from 1 to 5 carbon atoms per molecule is well known. This precipitation is usually carried out under conditions under which wax appears to be in true solution, and therefore the separation of asphalts and wax by this method was heretofore considered by many a more or less solved problem, which required little further development.

It has, however, been observed that asphalts produced from straight run i. e., uncracked waxy stocks by the above precipitation method frequently possess a cloudy appearance, abnormally low ductility and a positive Oliensis test. I have investigated the phenomenon which gives rise to these poor properties and have found that it is due to the presence of excessive amounts of certain types of paraffin waxes which are precipitated together with the asphalt. Since the Oliensis test is usually employed to detect the presence of deeply cracked residues in asphalts, and since moreover the precipitated asphalts with which this invention deals are substantially free from cracked components, the positive test must be caused by something other than cracked residues. The cause, as I have found, is wax. The presence of substantial amounts of wax in precipitated asphalts is rather unexpected, because normally the precipitation of the asphalt is carried out at temperatures well above incipient wax precipitation. In carrying out my investigation I have chosen the Oliensis test as a criterion by which to determine whether or not harmful amounts of wax are present in the precipitated asphalt. In relatively soft grades of asphalts this test correlates well with the other undesirable effects mentioned above of the wax. In the harder grades of asphalts, ductility is often difficult to measure, appearance is not reliable and the Oliensis test is the only remaining measure by which to recognize the presence of harmful wax. If the Oliensis test is negative, the asphalt is quite certain to be free from harmful amounts of wax.

The percentage of wax alone in an asphalt is no criterion whether the wax is harmful or not. Depending upon the system of the asphalt which comprises asphaltenes, maltenes, liquid oil, etc., different asphalts may have widely different capacities for retaining wax in harmless form. Moreover, I have discovered that there are at least two different types of paraffin wax, one which tends to be harmful even when present in very small amounts only, and the other which may be present in amounts many times the maximum permissible amount of the first type without harmful effect. The first type of wax is what may be called molecular aggregates of wax, as will be shown hereinafter.

I have found that when wax is precipitated from its solution in the course of ordinary dewaxing in the presence of liquefied normally gaseous hydrocarbons, the wax may come down either in the form of more or less individual crystals, or as large clusters of crystals in which the individual crystals are bonded together by a cement. This phenomenon has been described by Anderson and Talley in Industrial Engineering Chemistry, April 1937, pages 432 to 439. As shown in this publication heating the solution of wax prior to chilling, thereafter chilling it and precipitating the wax, leads to the formation of large wax clusters. The cement which is responsible for their formation comprises a resinous material, such as highly condensed aromatic hydrocarbons, adsorbed on wax. I believe that the heating influences the adsorption of this cement by disrupting dissolved molecular aggregates of wax to smaller aggregates or to individual molecules. The latter tend to adsorb more of the resins which may be contained in the oil, and upon precipitation of the wax, the wax particles containing the adsorbed resins form the cemented mass.

Now I have discovered that when heating hydrocarbon oils containing both wax and asphalts in substantial amounts, cooling the heated oil to an asphalt precipitating temperature above wax precipitating temperature, and precipitating the asphalt in the presence of normally gaseous hydrocarbons, an effect is experienced which seems contrary to that noted in dewaxing. In deasphalting, preliminary preheating results in the formation of precipitated asphalt containing wax in smaller amounts and in less harmful form than that contained in similar asphalts which are precipitated without preparatory preheating. Less harmful wax means wax which is contained in the asphalt in finer subdivision. Hence preheating causes the precipitated asphalt to contain wax in more finely divided form, whereas the effect

of preheating on dewaxing is to result in the formation of large clusters. Considering, however, the theory which explains the mechanism of the formation of wax clusters, based on a disruption of dissolved molecular wax aggregates, it is also possible to explain why preheating results in improved precipitated asphalts. The dissolved wax aggregates seem to behave like large molecules, the solubility of which in hydrocarbon oils is lower than that of individual wax molecules. Hence, not only will the amount of wax which is carried down with the precipitated asphalt be smaller after preheating than prior to preheating, but also its subdivision will be finer.

I have further found that wax aggregates disrupted by heating may reform upon standing in solution of liquid hydrocarbon oils at temperatures below those necessary to disrupt them. There appears to be a definite critical temperature for each solution above which the molecular aggregates are disrupted and below which they tend to rehabilitate, and the time required for this rehabilitation is normally of the duration of about one hour.

The critical temperature for the disruption of the molecular wax aggregates varies with the solvent, the exact relation between the amounts and properties of the solvents on the one hand and critical disruption temperature on the other hand being unknown at present. In the case of a typical Mid-Continent heavy residue, it is known that in the absence of added light hydrocarbons the critical temperature is above 200° or 250° F., and in the presence of two to four volumes of liquid propane or butane to said residue, the critical disruption temperature is about 160° F.

My invention thus comprises heating an asphalt-containing waxy petroleum oil to a temperature above that which is critical for the disruption of dissolved molecular wax aggregates, chilling the heated oil to the desired asphalt precipitation temperature, which temperature is above incipient wax precipitation temperature in the presence of asphalt precipitants, and within about one hour's time precipitating the asphalt with normally gaseous hydrocarbons. The heating may be carried out in the presence or absence of added solvents or asphalt precipitants. However, during heating the presence of asphalt precipitants, having critical liquefaction temperatures below about 160° F., e. g., methane and ethane, is not desirable, not only because of the enormous pressures which would develop upon heating the mixtures, but also because oily bodies are precipitated by heating above the critical temperature, which bodies are not desired in the asphalt and which normally are not completely redissolved upon cooling as disclosed in the Pier et al. U. S. Patent 2,055,135. Thus I limit the solvents or asphalt precipitants which may be present during the heating to those whose critical liquefaction temperatures are above the temperature which is critical for the disruption of the dissolved molecular wax aggregates.

The following examples serve to illustrate my invention.

Example I

A Mid-Continent waxy residue having the following properties:

Gravity A. P. I.	22.5
Flash °F. (A. S. T. M.)	460
Saybolt Univ. viscosity at 210° F. seconds	97
Pourpoint °F. (A. S. T. M.)	85

was deasphalted by the addition of four volumes of propane by three different procedures:

(1) Oil and propane were mixed at 120° F. and settled;

(2) Oil and propane were mixed at 160° F. and settled at 120° F.;

(3) Oil alone was heated to 250° F., cooled to 120° F. and immediately mixed with propane and settled at 120° F.

Results were as follows:

Procedure	Properties of asphalt				
	Percent wax (Holde)	Oliensis test	Penetration at 77° F.	Softening point, °F. (R & B)	Penetration index as defined in Nat. Pet. News Feb. 23, 1938
1	1.76	Positive	6	167	−0.3
2	1.32	Negative	1½	199	0.0
3	1.45	do	1	208	+0.1

It will be noted in the above table that by heating to 160° F. which is above the temperature necessary to disrupt the molecular wax aggregates, the Oliensis test became negative, whereas before that it was positive. Moreover as a result of this heating the wax content of the asphalt was lowered.

A precipitation temperature of 120° F. is well above incipient wax precipitation temperature as shown in the article on wax precipitation in Industral Engineering Chemistry of April 1937, previously referred to, in Figure 6 on page 434.

To determine the time within which the asphalt must be precipitated after heating in order to avoid rehabilitation of harmful wax aggregates which enter into the precipitate, the above residue was heated to 250° F. and was allowed to stand, samples being mixed at intervals with four volumes of propane and allowed to settle at 110° F. The following results were obtained:

Time of standing after heating to 250° F., hrs.	Properties of asphalt				
	Percent wax (Holde)	Oliensis test	Penetration at 77° F.	Softening point, °F. (R & B)	Penetration index
72	2.35	Positive	2	201	0.0
18	1.80	do	3	190	+0.3
12	2.18	do	3	185	0.0
1½	1.86	do	3	187	+0.1
1	1.50	Negative	2	193	0.0
½	1.55	do	1	208	+0.1

The above results indicate that wax aggregates had formed in about 1½ hours standing. To be on the safe side one should therefore effect the asphalt precipitation within about one hour's time after cooling to below the critical temperature of disruption of wax aggregates.

Since the settling temperature of 110° F. in the above example was slightly below that of incipient wax precipitation for the residue in the absence of propane, formation of visible wax was followed by visual examination under the microscope before mixing with the propane. At 1½ hours when the Oliensis test already proved to be positive no visible wax had separated, the first visible wax appearing after about 12 hours standing. This is proof that the presence of harmful wax aggregates in the precipitated asphalt is not due to preseparated wax in the oil from which the asphalt is precipitated.

In order to determine the critical disrupting temperature for the residual oil in the absence of

added hydrocarbons, three tests were carried out by heating same to three different temperatures, cooling, mixing at once with four volumes of propane and settling at 120° F.

Preheating temperature	Property of asphalt	
	Percent wax (Holde)	Oliensis test
160° F	2.18	Positive.
200° F	1.80	Do.
250° F	1.50	Negative.

The critical preheating temperature for the disruption of molecular wax aggregates according to the above is between 200° and 250° F.

Example II

A Mid-Continent waxy residue which previously had been freed from asphaltenes but containing maltenes had the following properties:

Gravity A. P. I.	23
Flash °F	440
Saybolt Univ. viscosity at 210° F. seconds	87
Pourpoint °F	85

This oil was dissolved in four volumes of butane. The resulting solution was perfectly clear and showed no sign of wax precipitation at 68° F. Three portions of this solution were pressured with natural gas at temperatures of 68°, 104° and 140° F., respectively, and a fourth portion was first dewaxed by chilling, and the dewaxed solution was then pressured at 68° F. Three progressively increasing pressures were applied to all four portions to effect precipitation of four approximately comparable sets of three cuts comprising asphaltic hydrocarbons. Since all four portions show no wax crystal formation at the lowest test temperature, the difference in the results tabulated below are not due to precipitated wax crystals, but are due to some other phenomenon, presumably relatively low solubility of the molecular aggregates.

Results were as follows:

Temperature	Cut	Property of asphalt				
		Penetration	Ductility	Percent wax	Oliensis test	Appearance
68° F	1	49	41	5.6	Positive	Very dull.
	2	61	54	4.8	do	Do.
	3	108	56	2.6	do	Do.
104° F	1	10	100+	2.7	do	Dull.
	2	41	100+	2.0	do	Slightly dull.
	3	171	100+	2.2	do	Do.
140° F	1	9	100+	1.7	Negative	Bright, shiny.
	2	156	100+	2.3	do	Do.
	3	200	100+	2.4	do	Do.
68° F. after dewaxing	1	6	100+	1.5	do	Do.
	2	36	100+	1.5	do	Do.
	3	134	100+	1.5	do	Do.

From the data in the above table it appears that for this petroleum oil the critical disruption temperature for wax aggregates in solutions of four volumes of butane is about 140° F. or slightly lower.

While in the foregoing I have disclosed a method for producing from waxy stocks precipitated asphalts free from harmful amount of wax aggregates, it is understood that fuel oils comprising asphalts may be produced in a similar manner for instance by direct precipitation or by diluting the precipitated asphalts with a suitable hydrocarbon oil. Such fuel oils which are substantially free from wax aggregates have pourpoints considerably lower than the fuel oils made from the same stocks by the same precipitation method but containing the wax aggregates. Moreover my method is useful in the production not only of asphalts which usually comprise mixtures of carboids, carbenes, asphaltenes, maltenes, resins, etc., but as shown by the examples is applicable as well for the manufacture of any one or of mixtures of two or more of the several components. Also so-called albino asphalts of the type described in my co-pending application Serial No. 186,133, filed January 21, 1938, now Patent No. 2,201,466, dated May 21, 1940, free from harmful wax, may be prepared in this manner. The term asphaltic hydrocarbons as herein used is meant to designate asphalt or components thereof, albino asphalt, etc.

I claim as my invention:

1. In the process of producing asphaltic hydrocarbons free from harmful wax from a straight run petroleum oil containing substantial amounts of both wax and said asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons, the improvement comprising adding to said oil an asphalt precipitating amount of 3 to 5 carbon hydrocarbons, heating the resulting mixture to a temperature not below that which is critical for the disruption of dissolved molecular wax aggregates in the presence of said 3 to 5 carbon hydrocarbons and which is lower than the critical liquefaction temperature of the added 3 to 5 carbon hydrocarbons, and cooling the mixture to an asphalt precipitating temperature above incipient wax precipitating temperature of the mixture, whereby asphalt free from harmful wax is precipitated, the time of cooling from said critical wax disruption temperature to said asphalt precipitating temperature being less than about one hour.

2. In the process of producing asphaltic hydrocarbons free from harmful wax from a straight run petroleum oil containing substantial amounts of both wax and said asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons, the improvement comprising adding to said oil an asphalt precipitating amount of 3 to 5 carbon hydrocarbons under conditions to produce a mixture having a temperature not lower than that which is critical for the disruption of dissolved molecular wax aggregates in the presence of said added 3 to 5 carbon hydrocarbons and which is lower than the critical liquefaction temperature of the 3 to 5 carbon hydrocarbons, and cooling the mixture to an asphalt precipitating temperature above incipient wax precipitating temperature of the mixture, whereby asphalt free from harmful wax is precipitated, the time

of cooling from said critical wax disruption temperature to said asphalt precipitating temperature being less than about one hour.

3. In the process of producing asphaltic hydrocarbons free from harmful wax from a straight run petroleum oil containing substantial amounts of both wax and said asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons, the improvement comprising adding to said oil an asphalt precipitating amount of propane under conditions to produce a mixture having a temperature between 160° F. and the critical liquefaction temperature of propane, and cooling the mixture to an asphalt precipitating temperature between 110 to 120° F., whereby asphalt free from harmful wax is precipitated, the time of cooling from 160° F. to the asphalt precipitating temperature being less than about one hour.

4. In the process of producing asphaltic hydrocarbons free from harmful wax from straight run petroleum oils containing substantial amounts of both wax and said asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons, the improvement comprising adding to said oil an amount of a 3 to 5 carbon hydrocarbon insufficient to effect a substantial precipitation of asphaltic hydrocarbons under conditions to produce a mixture having a temperature not lower than that which is critical for the disruption of dissolved molecular wax aggregates in the presence of said 3 to 5 carbon hydrocarbons but is lower than the critical liquefaction temperature of said 3 to 5 carbon hydrocarbons, and further adding an asphalt precipitating amount of a normally gaseous hydrocarbon under conditions to cool said mixture to an asphalt precipitating temperature above incipient wax precipitating temperature below said critical wax disruption temperature, whereby asphalt free from harmful wax is precipitated, the time of cooling from said critical wax disruption temperature to said asphalt precipitating temperature being less than about one hour.

5. In the process of producing asphaltic hydrocarbons free from harmful wax from a straight run petroleum oil containing substantial amounts of both wax and said asphaltic hydrocarbons by precipitation with normally gaseous hydrocarbons, the improvement comprising adding to said oil an amount of a 3 to 5 carbon hydrocarbon insufficient to effect a substantial precipitation of asphaltic hydrocarbons under conditions to produce a mixture having a temperature not lower than that which is critical for the disruption of dissolved molecular wax aggregates in the presence of said 3 to 5 carbon hydrocarbons but is lower than the critical liquefaction temperature of said 3 to 5 carbon hydrocarbons, and further adding an asphalt precipitating amount of natural gas under conditions to cool said mixture to an asphalt precipitating temperature above incipient wax precipitating temperature below said critical wax disruption temperature, whereby asphalt free from harmful wax is precipitated, the time of cooling from said critical wax disruption temperature to said asphalt precipitating temperature being less than about one hour.

ALVIN P. ANDERSON.