Nov. 24, 1942. H. E. CIER 2,303,023

PROCESS FOR PRODUCING IMPROVED ASPHALTS

Filed Dec. 19, 1940 3 Sheets-Sheet 1

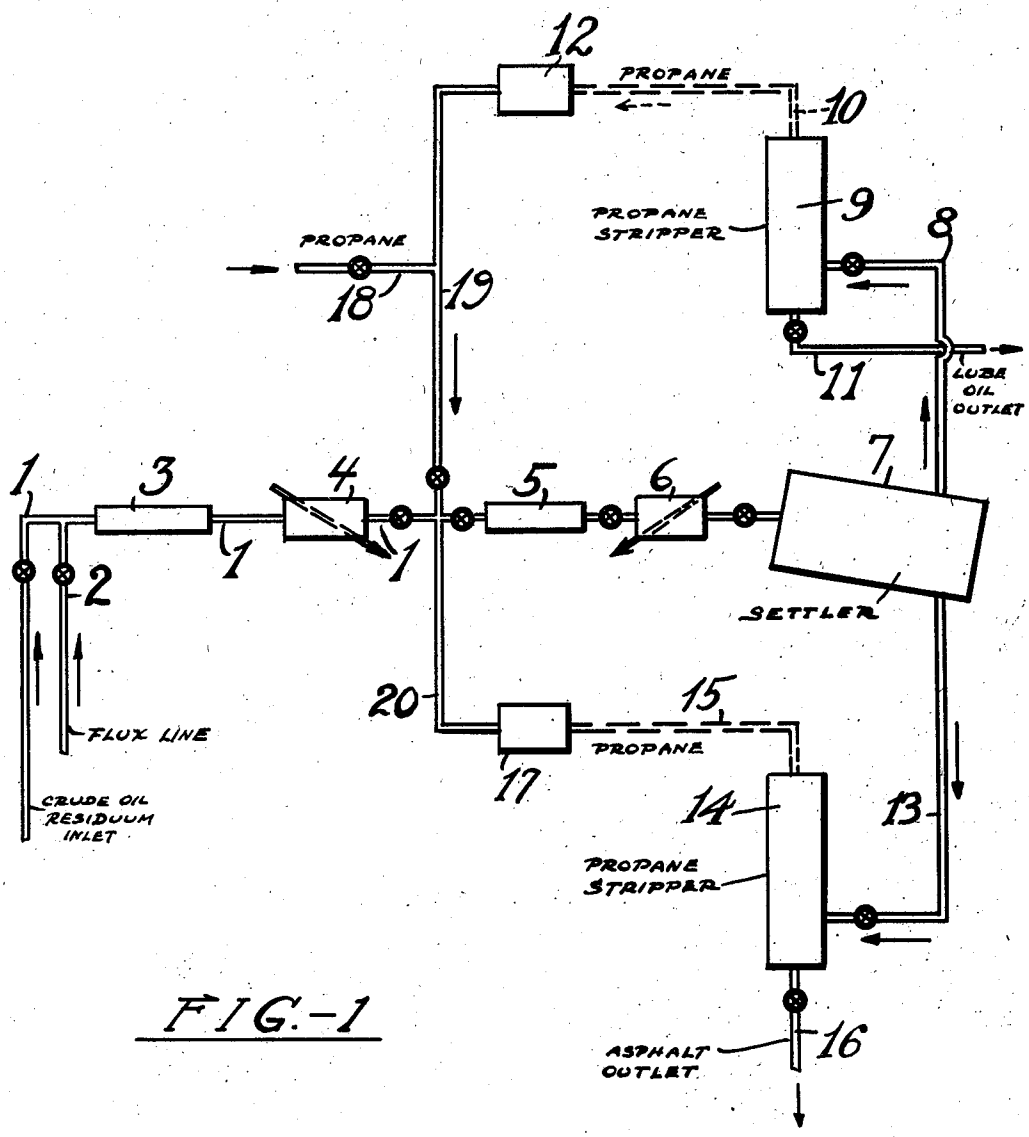


FIG.-1

Harry E. Cier Inventor

By J. C. Small Attorney

Nov. 24, 1942. H. E. CIER 2,303,023

PROCESS FOR PRODUCING IMPROVED ASPHALTS

Filed Dec. 19, 1940 3 Sheets-Sheet 2

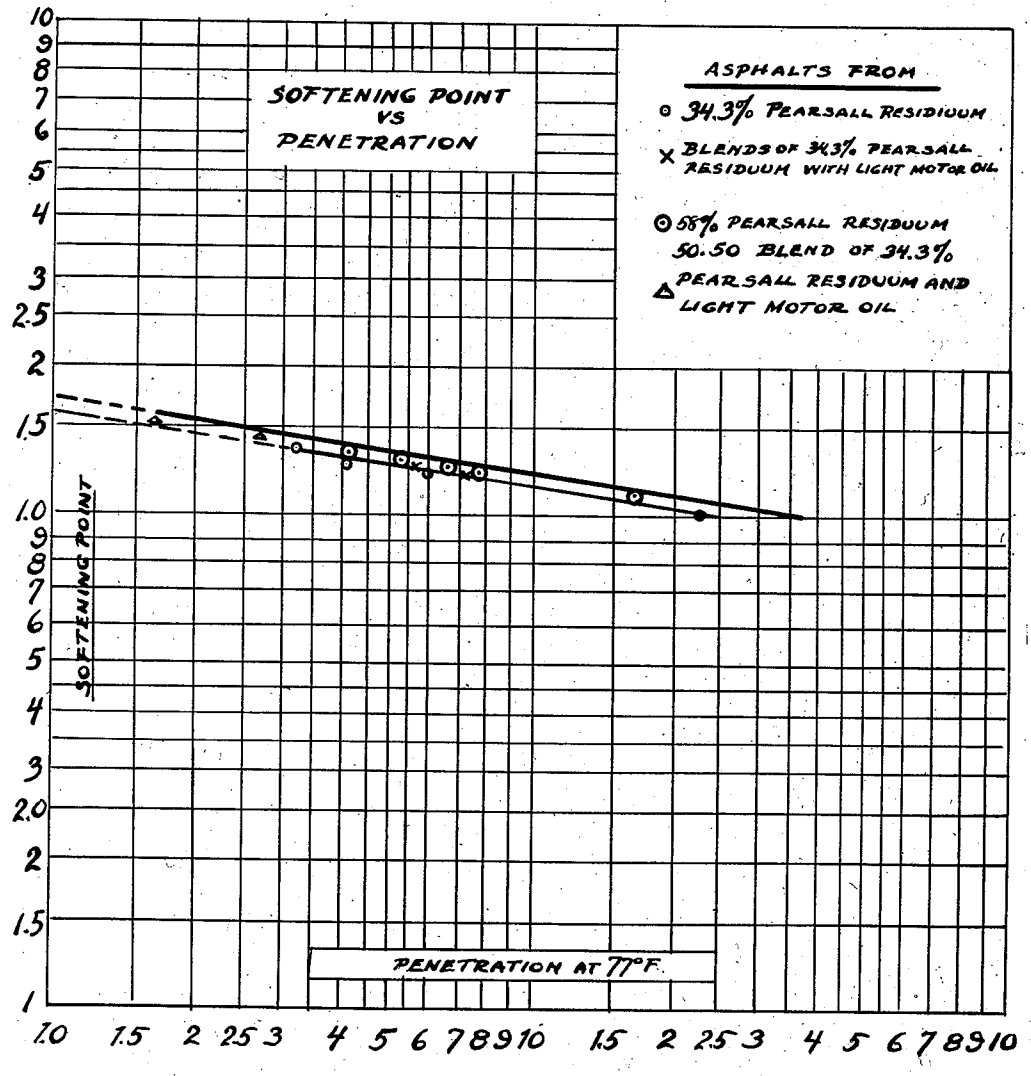


FIG.-2

Harry E. Cier Inventor
By J. E. Small Attorney

Nov. 24, 1942. H. E. CIER 2,303,023

PROCESS FOR PRODUCING IMPROVED ASPHALTS

Filed Dec. 19, 1940 3 Sheets-Sheet 3

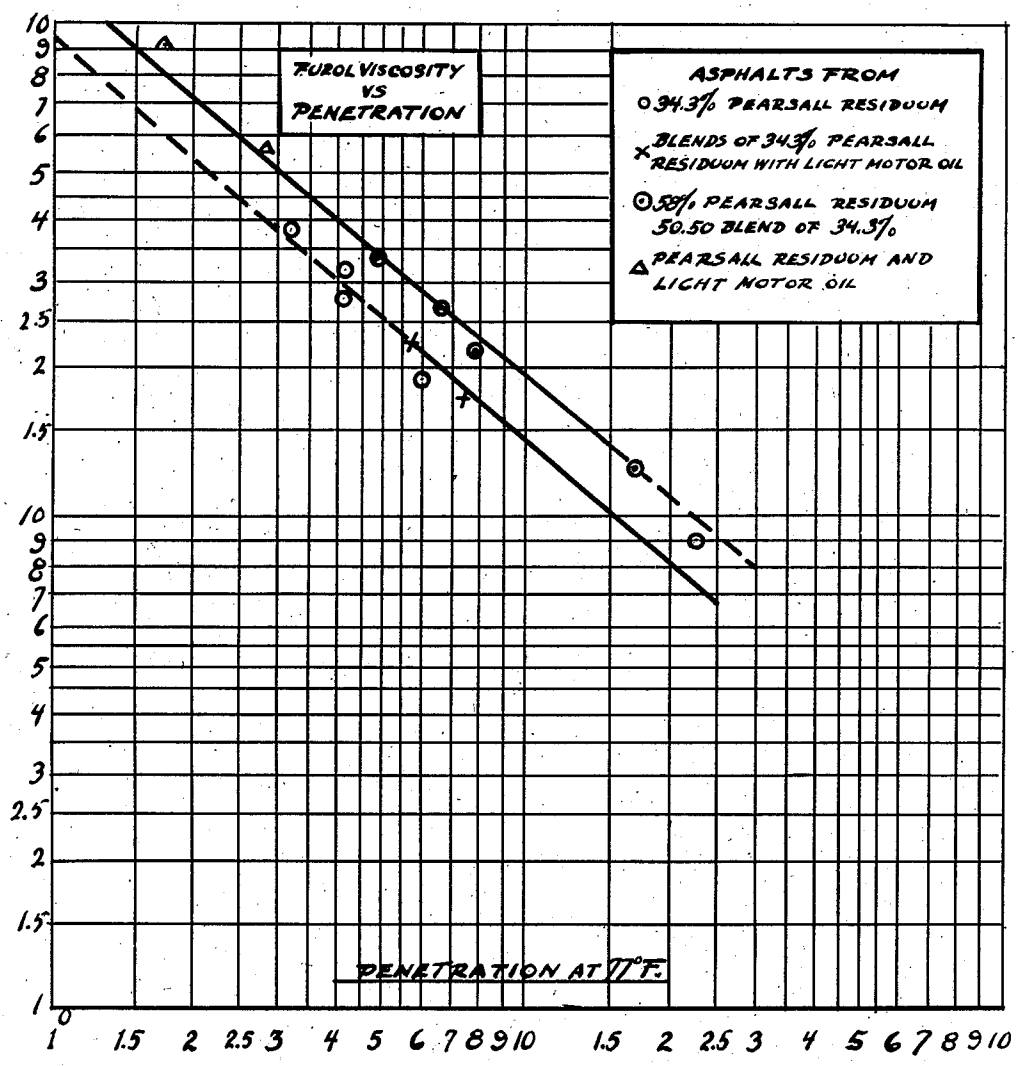


FIG. -3

Harry E. Cier Inventor

By J. C. Small Attorney

Patented Nov. 24, 1942 2,303,023

UNITED STATES PATENT OFFICE

2,303,023

PROCESS FOR PRODUCING IMPROVED ASPHALTS

Harry E. Cier, Baytown, Tex., assignor to Standard Oil Development Company, a corporation of Delaware

Application December 19, 1940, Serial No. 370,774

8 Claims. (Cl. 196—74)

This invention relates to a process for producing improved asphalts and more particularly, the invention is concerned with the production of asphalts having improved susceptibilities to temperature changes.

For many years different grades of asphalts have been prepared by blending asphalts of low penetration with naphthas, gas oils, and heavier fluxing agents. In fact, it is customary practice in the asphalt industry to prepare intermediate grades of asphalts by influxing a natural or oxidized asphalt with a suitable blend stock to produce an asphalt of proper specifications. It is also well known in the art to dilute a crude residuum with a liquefied normally gaseous hydrocarbon and, by proper adjustment of temperature, to throw out or precipitate from the oil solution an asphalt which is suitable, after fluxing with a lighter oil or asphalt, for use in road building or in manufacture of other material for which asphalt has been adapted.

Propane precipitated asphalts when blended to specification usually result in good quality products. Moreover, by the propane precipitation and fluxing method it is possible to produce a wide range of products. However, these conventionally produced asphalts frequently have a high softening point-penetration index and a relatively low fluidity index or vice versa. It is desirable, however, for asphalts to have both high softening point-penetration and fluidity indexes, since one index indicates the consistency at normal temperatures whereas the other index is a measure of consistency at elevated temperatures. In short, these indexes for asphalt may be compared to the viscosity index for lube oils. The softening point-penetration and fluidity indexes are described by Holmes, Collins and Child ("Measuring the susceptibility of asphalt to temperature changes"—Holmes, Collins and Child, Ind. & Eng. Chemistry, Analytical Edition, vol. 8—pages 100–104, March 15, 1936), who arbitrarily assigned a value of 100 for asphalts from Mexican crude and 0 for asphalts from cracking coil tar.

The softening point-penetration index is a relationship existing between the penetration of an asphalt at 77° F. and the ring and ball softening point. The method of test for determining the penetration of an asphalt is described in the 1939 Book of A. S. T. M. Standards including Tentative Standards, Part III, under the A. S. T. M. designation D5—25. The softening point, by the ring and ball method, is also described in the aforementioned reference under A. S. T. M. designation E28—39T.

The relationship existing between the penetration and softening point may be expressed by the equation

$$M=kP^a$$

where M is the ring and ball softening point in °F., P the penetration, and a and k are constants depending on the source of the asphalt and the temperature at which the penetration is taken.

The fluidity index is a similar relationship existing between the penetration at 77° F. and Saybolt Furol viscosity at 275° F. It measures the susceptibility of the asphalt to consistency changes at elevated temperatures, whereas the softening point-penetration index is an indication of the temperature susceptibility of an asphalt at normal temperatures (77° F.).

It is an object of this invention to produce an asphalt that will not soften to a great degree when used as a filler in either wood or stone block pavement. An asphalt that will soften under normal summer conditions and which will ooze out of the joints onto the paving blocks is undesirable and objectionable. It is a further object of this invention to produce an asphalt that, while it will not soften and flow under usual summer conditions, is sufficiently fluid under suitable conditions of heating to be used in paving mixtures and in road surfacing compositions where it is necessary that the aggregate be coated with binder to produce a coherent adhesive mass.

It has now been discovered that, if a crude residuum is fluxed with a heavy oil fraction and is then diluted with propane, an asphalt of improved temperature susceptibility characteristics may be obtained. It was also found that asphalts produced by fluxing the residuum prior to propane precipitation are vastly superior in quality to asphalts produced by propane precipitation followed by fluxing. For asphalts of equivalent penetration this product, produced in the manner which will be further described in detail, has higher susceptibility indexes than are obtained either by conventional propane precipitation or by conventional propane precipitation followed by fluxing. In general this invention may be described as follows: a crude petroleum is reduced by distillation to a residuum having a minimum Saybolt Universal viscosity of about 400 seconds at 210° F. While it is preferred to reduce the crude to what is termed in the art a "short residuum," it may also be reduced to a long residuum. After reducing the crude to the minimum viscosity required the residual crude may be fluxed with a lubricating oil fraction which

is not a fraction of the same reduced crude. On the other hand, in some instances, it is preferred to deasphalt a long residuum which, in effect, is fluxing a short residuum with a contiguous fraction of the same crude. In either instance, however, the fluxed residuum is diluted with about four to five volumes of a liquefied normally gaseous hydrocarbon; while it is preferred to employ propane as the solvent, any hydrocarbon fraction such as ethane, propane, butane, pentane and the like or mixtures of these fractions which will allow precipitation of asphalt from solutions thereof may be employed. The propane-oil solution is cooled to a temperature where asphalt and resinous material will precipitate and is then introduced into a suitable settling drum where asphaltic and resinous material separate from the solution as a bottom layer. The asphalt is drawn off from the soluble oil and propane layer, may be washed with additional amounts of propane, and is then stripped of residual solvent. The solvent-free asphalt is then suitable for use in road building or otherwise as may be desired.

In the accompanying drawings, Figure 1 represents a general flow diagram of the process; Figure 2 a softening point-penetration graph; and Figure 3 a furol viscosity-penetration graph.

With reference to Figure 1 which represents a flow diagram of one embodiment of this invention, a heavy lubricating oil flux is introduced through line **2** into line **1** through which a crude oil residuum fraction is being charged by means of a pump not shown. The two oils are thoroughly mixed in incorporator **3** and are then heated to between about 120° F. to 180° F. in heating means **4**. The heated fluxed residuum is then diluted with liquid propane which is introduced through lines **19** and **20**; make-up propane, when needed, may be injected into the system through line **18**. The fluxed oil and propane are thoroughly mixed in incorporator **5** and the temperature of the resulting propane-oil solution is adjusted to about 110° F. to 150° F. in heat exchanger **6** from whence the mixture flows into asphalt settler **7** which is preferably maintained at a temperature of about 110 to 130° F. However, the temperature of the asphalt in the settler may be maintained either higher or lower than the limits mentioned since the penetration of the precipitated asphalt is controlled by the precipitation temperature in the asphalt settler. An oily-propane solution is drawn off of settler **7** by means of line **8** into propane stripper **9** where solvent and lubricating oil are recovered. Vaporized propane from stripper **9** is returned to the system through line **10**, liquefication means **12**, and line **19**. Deasphalted lubricating oil is drawn off of the bottom of stripper **9** through line **11** to storage. Asphalt is drawn off of the bottom of settler **7**, through line **13**, into propane stripper **14** where the asphalt is stripped of residual propane, the propane stripped from the asphalt being recycled to the charge system by means of line **15**, liquefication means **17**, and line **20**. Asphalt of improved quality is drawn off to storage from the bottom of stripper **14** through line **16**.

Although the mechanism of the solvent action, resulting in the improvement in asphalt temperature susceptibilities, wrought by fluxing of the residuum prior to propane precipitation of asphalt therefrom is not clearly understood, it is postulated that by fluxing the crude residuum prior to propane precipitation, poor fractionation between the predominantly oily and the predominantly asphaltic constituents occurs. This is a desirable rather than an undesirable condition, since it is further theorized that the undesirable components in the oil or asphalt employed as a fluxing medium, which normally impart poor susceptibility to the mixture, are dissolved in the solvent, whereas those components which contribute toward good susceptibility are included with the precipitated asphalt. Thus, in effect according to these theories, the ratio of oils to resins in the asphalt produced in accordance with this invention has been increased over that contained in asphalt produced by conventional propane precipitation followed by fluxing. It is to be clearly understood, however, that this invention is not to be limited by any theories which may be advanced in explanation of the improved result.

In order to more clearly describe this invention, reference is made to the following examples:

Example 1

A sample of crude oil from the Pearsall field in Texas was reduced by distillation to 34.3% bottoms. This residual fraction from the crude had the following characteristics:

Specific gravity at 60° F	1.005
Open cup flash, ° F	610
Furol viscosity at 275° F	91
Pen. at 77° F., 100 g., 5 sec	232
Ring and ball softening point, ° F	104
Ductility at 77° F	110+
Solubility in CCl_4	99.69
Oliensis test	Negative

The 34.3% bottoms fraction having the above inspection characteristics was subjected to a series of deasphalting treats in which one volume of reduced crude to four volumes of propane of 96% minimum purity was employed. Temperatures between 120° F. and 140° F. were employed in the treats. The asphalt obtained from these treats were tested and the following inspection data were obtained:

	Treat 1	Treat 2	Treat 3
Deasphalting temp., °F	120	130	140
Asphalt yield, wt. per cent on charge	69.6	70.4	82.6
Specific gravity at 60° F	1.050	1.025	1.034
Open cup flash, °F	615	620	615
Furol viscosity at 275° F	381	280	191
Pen. at 77° F., 100 gms., 5 sec	32	41	60
Ring and ball softening point, °F	135	128	122
Ductility at 77° F	110+	110+	110+
Solubility in CCl_4, per cent	99.57	99.73	99.74
Oliensis test	Neg.	Neg.	Neg.

The sample of Pearsall crude residuum representing 34.3% bottoms on the original crude was then fluxed with a fraction from the same crude representing a 42–65.7% fraction. The blended residual fraction representing 58% bottoms on the crude had the following inspection characteristics:

Specific gravity at 77° F	0.958
Open cup flash, ° F	385
Furol viscosity at 122° F	572
Per cent asphalt of 100 penetration	74.8

The fluxed bottoms fraction having the above-described physical characteristics was also subjected to a series of deasphalting treats in which one volume of fluxed reduced crude to four volumes of propane was employed. The propane diluent ranged between 87.4 and 96% by volume minimum purity. Distillation analyses of the

propane diluent showed the impurities to consist mainly of ethane and a small quantity of butanes. Thus for example, the analysis of the 87.4% propane diluent was as follows: Ethane 12.4%, propane 87.4%, butanes 0.2%. Temperatures between 120° F. and 140° F. were employed in the propane precipitation of asphalt. The asphalts obtained from the treats of the fluxed residual fraction were tested and were found to have the following characteristics:

	Treat 4	Treat 5	Treat 6	Treat 7	Treat 8
Deasphalting temp., °F.	120	140	120	130	140
Asphalt yield, wt. per cent based on charge	40.5	46.0	38.5	39.5	45.5
Specific gravity at 60° F.	1.035	1.019	1.042	1.033	1.041
Open cup flash, °F.	425	425	420	425	430
Furol viscosity at 275° F.	339	127	320	269	222
Pen. at 77° F., 100 gms., 5 sec.	48	165	41	66	77
Ring and ball softening point, °F.	130	111	133	126	123
Ductility at 77° F.	110+	110+	110+	110+	110+
Solubility in CCl_4, per cent	99.75	99.74		99.67	99.62
Oliensis test	Neg.	Neg.	Neg.	Neg.	Neg.

It will be noted on comparing the data obtained on the asphalt from treat 2 with that from treat 6 that, for an equivalent penetration, the flash on the asphalt obtained in treat 6 is 200° F. lower than that obtained in treat 2 indicating that this asphalt contains lighter material than the asphalt from treat 2. It is this lighter material which imparts the desired temperature susceptibility qualities which are readily apparent from a further study of the data.

The softening point and penetration data obtained in treats 1 to 7 were then plotted on 2 cycle logarithmic graph paper with the ordinate representing the ring and ball softening point and the abscissa representing penetration at 77° F. These data are presented graphically in Figure 2. After plotting the data as described herein, softening point values for asphalts having penetrations ranging between 50 and 200 in 50 point intervals were obtained. Thus, an asphalt obtained by conventional propane precipitation (treats 1 to 3) having a penetration of 100 would have a softening point of 115° F. By means of the softening point-penetration index chart devised by Holmes, Collins, and Child, a value of 80 is obtained as the softening point index for an asphalt having those particular penetration and softening point inspection characteristics. Similarly, the following data were obtained:

Penetration at 77° F.	Softening point-penetration index	
	Conventionally produced asphalt (treats 1-3)	Asphalt produced in accordance with this invention (treats 4-8)
50	62	89
100	80	110
150	85	130
200	100	150+

In a similar manner, the furol viscosity of the asphalts from the several aforementioned treats were plotted as ordinates on logarithmic graph paper against penetration at 77° F. as the abscissa. These data are presented graphically in Figure 3. Then by recourse to the Fluidity index chart also constructed by Holmes, Collins, and Child, fluidity indexes for asphalts having 50, 100, 150, and 200 penetration were obtained.

Penetration at 77° F.	Fluidity index	
	Conventionally produced asphalt (treats 1-3)	Asphalt produced in accordance with this invention (treats 4-8)
50	78	88
100	73	87
150	68	85
200	67	85

On comparing the physical properties, as measured by softening point-penetration and fluidity indexes, of asphalt produced in accordance with this invention with that produced by conventional propane precipitation, it is readily apparent that this improved process produces asphalts of greatly improved temperature susceptibility characteristics.

Example 2

A residual fraction representing 34.3% bottoms on Pearsall crude was deasphalted at 120° F. employing four volumes of propane to one volume of the bottoms fraction. The resulting asphalt, which corresponds to that obtained in treat 1 shown in Example 1, was then fluxed with a light motor oil to produce asphalts of different penetrations.

	Blend 1	Blend 2	Blend 3
Asphalt, wt. percent	100	95	92.5
Light motor oil, wt. percent	0	5	7.5
Furol viscosity at 275° F.	381	229	182
Pen. at 77° F., 100 gms., 5 sec.	32	57	72
Ring and ball softening point, °F.	135	125	121

The softening point and penetration data obtained on inspections of the blends was then plotted on logarithmic graph paper and are shown in Figure 2. Softening points for asphalts having penetrations of 50, 100, 150, and 200 were then read off. Again referring to the softening point-penetration index chart of Holmes, Collins, and Child, indexes as follows were obtained for asphalts having the mentioned specifications:

Penetration at 77° F.	Softening point-penetration index	
	Asphalt produced by propane precipitation and fluxing	Asphalt produced in accordance with this invention
50	62	89
100	80	110
150	85	130
200	100	150+

On comparing the data in Example 1 with the above results it will be noted that identical values were obtained by conventional propane precipitation and by propane precipitation followed by fluxing. The asphalts produced in accordance with this invention, i. e., fluxing followed by propane precipitation, however, are superior in temperature susceptibility (as measured by the softening point-penetration index) to either of the two conventional methods. Similar advantages are shown for asphalts obtained by my im-

proved method when fluidity indexes are compared.

Example 3

A residual fraction representing 34.3% bottoms on Pearsall crude was blended with equal volumes of a light motor oil. Inspection characteristics of the Pearsall bottoms fraction are shown in Example 1. The light motor oil was tested and had the following characteristics:

Specific gravity	0.8783
Open cup flash, °F	450
Open cup fire, °F	530
SSU viscosity at 210° F	50.3

The resulting blend of motor oil and Pearsall bottoms was deasphalted at 120° F. and 140° F. to obtain different penetrations of asphalt. One volume of blend to four volumes of propane was employed.

The asphalt precipitated at 120° F. and 140° F. was freed of propane and the following test data were obtained:

	Asphalt precipitated at 120° F.	Asphalt precipitated at 140° F.
Furol viscosity at 275° F	924	574
Pen. at 77° F., 100 gms., 5 sec.	17	28
Ring and ball softening point, ° F	153	142
Open cup flash, ° F	520	525

These data were then plotted on Figures 2 and 3 to which reference has been made. The softening points were plotted as ordinates and the penetrations as abscissae on Figure 2. It will be noted that these data follow the curve plotted from the data on asphalt obtained from treats 4 to 8 in Example 1.

In a similar manner, the furol viscosities at 275° F. were plotted against penetrations on Figure 3. It will again be noted that the data follow the curve for the asphalts precipitated in treats 4 to 8 rather than the curve for asphalts from treats 1 to 3 presented in Example 1.

These data demonstrate that asphalts of superior temperature susceptibility may be produced in accordance with this invention of fluxing the residuum prior to propane precipitation rather than afterwards. The data also clearly show that the flux need not be a contiguous fraction of the same crude from which the asphalt is obtained. This is important since it may be desirable in some instances to flux the residual fraction with a low grade product for which no ready market exists.

I claim:

1. Process for producing asphalts having improved susceptibility characteristics to temperature changes comprising the steps of fluxing a reduced crude with a low viscosity hydrocarbon fraction boiling within the lubricating oil range, diluting with a liquefied gaseous hydrocarbon, adjusting the temperature so that an asphalt is precipitated therefrom, separating said precipitated asphalt from that portion soluble in the diluent and stripping said precipitated asphalt free of light hydrocarbons.

2. Process for producing asphalts having improved susceptibility characteristics to temperature changes comprising the steps of fluxing a reduced crude with a low viscosity hydrocarbon fraction boiling within the lubricating oil range, diluting said fluxed reduced crude fraction with a liquefied normally gaseous hydrocarbon, adjusting the temperature of said diluted, fluxed reduced crude fraction so that an asphalt is precipitated therefrom, separating said precipitated asphalt from that portion of the fluxed reduced crude fraction soluble in the diluent, freeing said separated asphalt of entrained oil fractions by washing same with additional quantities of liquefied normally gaseous hydrocarbon solvent, stripping said washed asphalt free of light hydrocarbons in a stripping still, and recovering therefrom an asphalt of improved temperature susceptibility characteristics.

3. Process in accordance with claim 2 in which the liquefied normally gaseous hydrocarbon is propane.

4. Process in accordance with claim 2 in which the fluxing agent is blended with the residual crude fraction in the ratio of 0.2–2.5 volumes of flux to one volume of residual crude fraction.

5. Process in accordance with claim 2 in which the fluxing agent is an unfinished lubricating oil fraction.

6. Process for producing asphalt having improved susceptibility characteristics to temperature changes which comprises the step of reducing a crude to a minimum Saybolt Universal viscosity of about 400 seconds at 210° F., fluxing the reduced crude with a low viscosity hydrocarbon fraction boiling within the lubricating oil range, diluting with a liquefied gaseous hydrocarbon, adjusting the temperature so that an asphalt is precipitated therefrom, separating said precipitated asphalt from that portion soluble in the diluent and stripping said precipitated asphalt free of light hydrocarbons.

7. Process of producing asphalt having improved susceptibility characteristics to temperature changes which comprises the steps of reducing the crude to a minimum Saybolt Universal viscosity of about 400 seconds at 210° F., fluxing the reduced crude with a low viscosity hydrocarbon fraction of the same crude boiling within the lubricating oil range, diluting with a liquefied gaseous hydrocarbon, adjusting the temperature so that an asphalt is precipitated therefrom, separating said precipitated asphalt from that portion soluble in the diluent and stripping said precipitated asphalt free of light hydrocarbons.

8. Process of producing asphalt having improved susceptibility characteristics to temperature changes which comprises the steps of reducing by distillation an asphaltic crude to a residuum having a minimum Saybolt Universal viscosity of about 400 seconds at 210° F., fluxing the residuum with a low viscosity hydrocarbon of a different crude boiling within the lubricating oil range, diluting said fluxed reduced residuum with a liquefied normally gaseous hydrocarbon, adjusting the temperature so that an asphalt is precipitated therefrom, separating said precipitated asphalt from that portion soluble in the diluent and stripping said precipitated asphalt free of light hydrocarbons.

HARRY E. CIER.