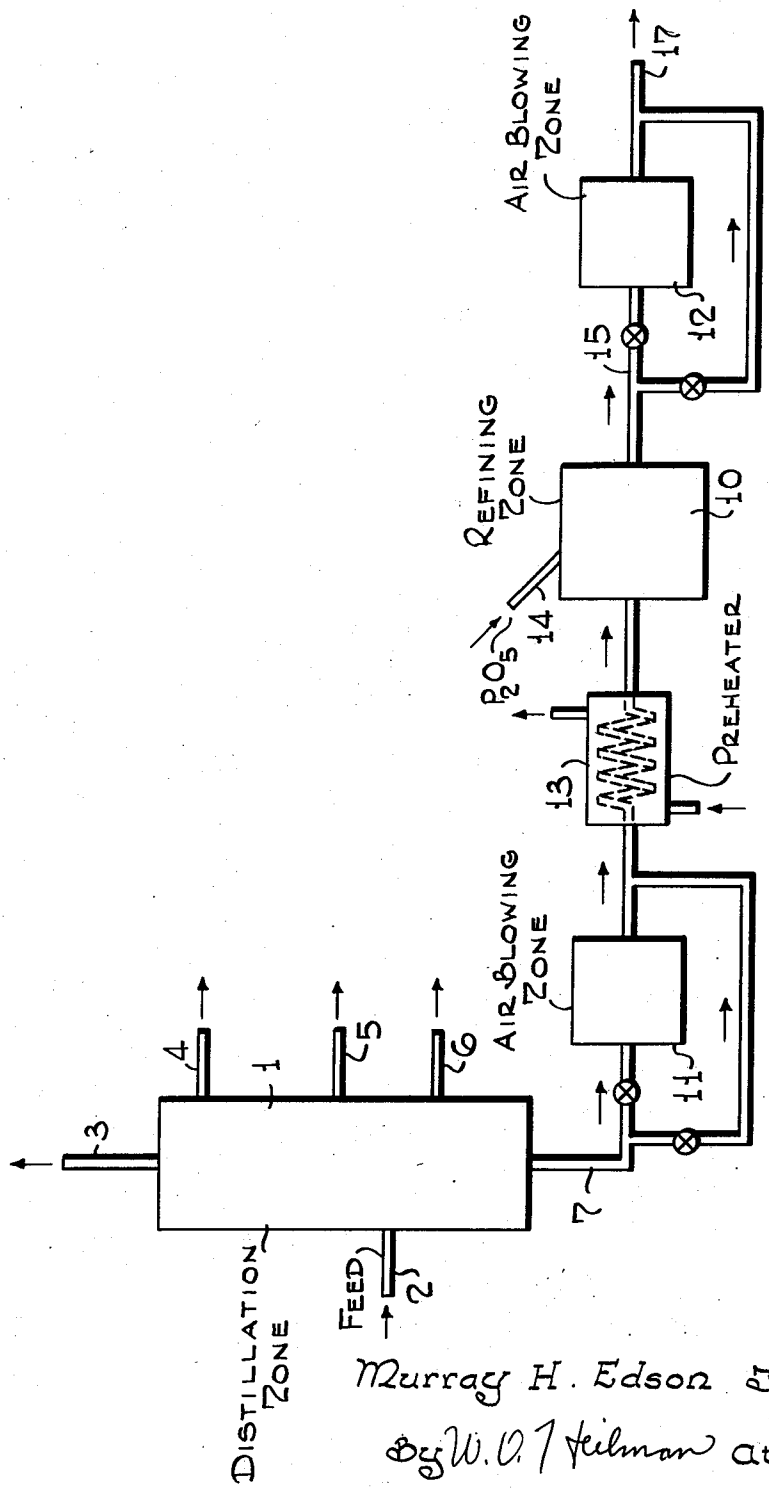
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PROCESS FOR PRODUCING AND REFINING ASPHALT

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PROCESS FOR PRODUCING AND REFINING ASPHALT

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This invention concerns a novel process for treating residual oils and hydrocarbon residues, to obtain asphalts of desirable properties. The process employed depends upon a heat treatment of the residual oil in the presence of P_2O_5. This process can in many cases be advantageously varied by air blowing the residual oil prior to contact with P_2O_5, or by air blowing the asphalt obtained by treatment of residual oil with P_2O_5. While as indicated, the process is particularly adapted for the treatment of residual oils to recover asphalts therefrom; the process may also be employed for the upgrading of asphalts obtained by conventional processing steps.

The present invention concerns the recovery of asphalts and the refining of asphalts obtained from petroleum oils. The principal objective of the process herein disclosed is to provide asphalts having unusual properties; in particular, asphalts are obtained which have usually high penetration and ductility properties for a given softening point, although, as will be brought out, other desirable properties may also be realized. This unusual combination of characteristics is demanded in a number of applications, an outstanding example of which is the lining of irrigation canals. Asphalts employed to line irrigation canals ideally should have properties to enable the asphalt lining to retain its shape in hot weather, to be non-brittle in cold weather, and to conform to the contour of the surface of the canal without tearing. Asphalts having these properties must have a softening point of about 175° to 200° F., and must have high ductility and high values of penetration. It has been found that asphalts obtained by conventional processing methods do not have the necessary combination of properties. More precisely, the asphalts obtained by conventional processing techniques, in the range of softening points identified, have too low a ductility and too low a penetration to meet the desired characteristics.

It is therefore the principal object of this invention to provide an asphalt recovery and treating process which will vary the usual combination of softening point, penetration, and ductility properties. To bring out the manner in which these asphalt properties are affected, it is helpful to consider the results of subjecting crude residua to an oxidation treatment as achieved by conventional air blowing. Oxidation treatments of this character are well known to the art and it has been appreciated that the low temperature susceptibility of asphalts may to some extent be improved by oxidation. However, when air blowing is applied and continued, while the softening point of an asphalt is raised, the penetration is decreased and the ductility is

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lowered. Consequently, contra to this change in asphalt properties, the process of this invention provides an increase in penetration properties and an increase in ductility concomitant with the increase in softening point of the asphalt.

The process by which these desirable changes in asphalt properties are obtained depends upon the catalytic treatment of residual oils or asphalts with P_2O_5. The precise mechanism of the asphalt change which occurs is not understood, although the principal effect appears to depend upon polymerization and condensation reactions. It is important to note that the treatment is in no respect an oxidation treatment, and in fact oxidation or the presence of air during the process is to be avoided. Thus, it has been determined that for the purposes of this invention, degradation in asphalt quality results from the presence of air during treatment with the P_2O_5.

The quantity of P_2O_5 to be employed ranges from about 0.1 to 5% by weight. The precise amount of P_2O_5 to be used depends principally upon the properties desired and the starting materials. In all cases treatment with P_2O_5 is preferably continued until equilibrium has been obtained. As the P_2O_5 treatment of asphalt proceeds readily, the time required is reasonably short and does not ordinarily exceed one hour. The temperature of treatment with P_2O_5 is chosen from the range of 300° to 550° F. Again, the precise temperature to be used depends to some extent upon the asphalt characteristics desired and the starting materials.

This treatment of a residual oil or an asphalt with P_2O_5 at 300° to 550° F. in the absence of air or oxygen produces a material change in the properties of the asphalt. In particular, the softening point of the asphalt is raised and the temperature susceptibility of the asphalt is improved to values otherwise unobtainable.

While as indicated, the critical treatment with P_2O_5 depends upon the exclusion of any oxidation effects, it has been found valuable in certain applications to employ an oxidation treatment either before or after, but not simultaneously with the P_2O_5 treatment. One adaptation of the process of this invention therefore depends upon oxidizing an asphalt followed with P_2O_5 treatment in the absence of air; another adaptation of the process utilizes P_2O_5 treatment in the absence of air followed by an oxidation treatment. Both of these adaptations causes a variation in asphalt properties different from those which occur without the oxidation treatment or when the oxidation is applied simultaneously with the P_2O_5 treatment. Furthermore, the oxidation treatment when applied before or after

the P_2O_5 treatment, decreases the amount of P_2O_5 required to attain a particular softening point.

To fully disclose the nature of this invention, reference will be made to the accompanying drawing which diagrammatically illustrates a flow plan of a preferred process embodying this invention. The process illustrated in the drawing concerns the preparation of asphalt from a residual oil obtained by distillation of a crude petroleum oil, although it is to be understood that the process illustrated may be applied to asphalts which may be obtained by other methods. The term "residual oils" by definition is employed to identify the liquid or semi-solid residues obtained from the destructive distillation of non-asphaltic petroleum, from the distillation of semi-asphaltic and asphaltic petroleums, from the distillation of pressure tar, or from the fluxing of harder residual asphalts with heavy distillates. The term "flux" or "flux oil" may be used synonymously with the term "residual oil."

By way of example, in the process illustrated in the drawing, a residual oil is obtained in distillation zone 1 by treatment of a semi-asphaltic or asphaltic petroleum oil introduced to still 1 through line 2. Normally gaseous hydrocarbons may be withdrawn from distillation zone 1 through line 3, while side stream products consisting of gasoline, kerosene, gas oil, lubricating oil, etc., may be withdrawn through lines 4, 5, 6, etc. The residual oil may be removed as the bottoms produce from the distillation zone through line 7 and will include substantially all of the asphaltic constituents originally present in the crude oil distilled. The specific gravity of the residual oil at 77° F. will range from about 0.85 to 1.07, and the fusing point of the oil as determined by the ring and ball method will generally fall within the range of 32° to 120° F. This residual oil may be converted to an asphalt of desirable properties by the processing sequence illustrated in the drawing.

As will be brought out, the primary and essential treatment of the residual oil depends upon a catalytic treatment with P_2O_5 in refining zone 10. Use of the two air blowing zones 11 and 12 is optional and for simplicity it may be assumed that zones 11 and 12 are by-passed by the by-pass lines provided. In this case the residual oil withdrawn from distillation zone 1 through line 7 will preferably be passed through a pre-heater 13 and will then be introduced directly into refining zone 10. Sufficient P_2O_5 is introduced to zone 10 through line 14 to provide a weight percent of about 0.1 to 5%. Mechanical agitation by inert gases such as nitrogen is employed in zone 10 to thoroughly mix the residual oil and P_2O_5. By suitably preheating the residual oil in preheater 13 and/or by utilizing heating jackets, steam coils, etc., in zone 10, mixing in zone 10 is carried out at a temperature in the range of 300° to 550° F. Care is taken to exclude air or oxygen from zone 10. As a result, with this treatment of P_2O_5, the softening point of the asphalt is increased and other properties of the asphalt are changed. The ultimate properties obtainable are dependent upon the particular temperature of treatment, the percentage of P_2O_5 employed, and the initial flux oil treated. Prior to reaching equilibrium properties, the time of treatment will also affect the asphalt properties. However, it is important to continue the mixing until no further change in properties occurs. This can be readily determined by periodically determining the softening point, the penetration or other inspections of the asphalt during treatment. In general, about 30 to 90 minutes are to be employed for the P_2O_5 treatment, depending upon starting material, temperature, quantity of change, amount of P_2O_5, and degree of agitation. The final asphalt product may then be removed from zone 10 through line 15.

As will be demonstrated, in some cases it is preferred to air blow the residual oil or asphalt prior to the P_2O_5 treatment. In this case the residual oil of line 7 is introduced to zone 11 for contact with an oxidation agent such as air. The oxidation treatment may be conducted in any desired manner; for example, by blowing about 30 to 50 cu. ft. of air per minute per ton of asphalt through the residual oil at about 300 to 550 F. temperature. Thereafter the air blown oil may be withdrawn from zone 11 and passed through preheater 13 for treatment with P_2O_5 in zone 10 as described. The final asphalt product is then obtained by withdrawing the asphalt directly from zone 10 through line 15.

Rather than applying the oxidation treatment prior to P_2O_5 treatment, it is sometimes preferred to apply the oxidation treatment after the P_2O_5 treatment. In this case the residual oil of line 7 will by-pass zone 11 and will be subjected to P_2O_5 treatment in zone 10. Thereafter the asphalt removed from zone 10 through line 15 will be passed to oxidation zone 12 wherein a treatment similar to that applied in oxidation zone 11 will be employed. In this case the final asphalt product will be withdrawn from line 17.

To exemplify the operability and utility of the process described, the following examples are presented, showing the properties of asphalts obtainable.

EXAMPLE I

As typical of the asphalts obtained by the conventional reduction of residual oils a Venezuelan crude oil was subjected to vacuum reduction providing an asphalt of the following properties:

Table I.—Vacuum reduced asphalt

Flash point (Cleveland open cup)---° F.	485
Softening point (ring and ball)---° F.	90
Penetration at 77° F., 100 grams, 5 sec. $\frac{mm.}{10}$	300+
Penetration at 32° F., 200 grams, 60 sec. $\frac{mm.}{10}$	95
Penetration at 115 ° F., 50 grams, 5 sec. $\frac{mm.}{10}$	300+
Ductility at 77° F., cm	125
Furol viscosity at 210 °F., seconds	345

After an oxidation treatment as provided by air blowing, an asphalt of the character identified in Table I has the following typical properties provided by different degrees of oxidation A, B and C.

Table II.—Oxidized reduced asphalt

	A	B	C
Flash Point (Cleveland Open Cup), ° F	530	510	585
Sofenting Point (Ring and Ball), ° F	195	226	291
Penetration at 77 ° F./100 gms./5 sec	29	16	5
Penetration at 32 ° F./200 gms./60 sec	18	11	2
Penetration at 115 ° F./50 gms./5 sec	45	31	6
Ductility at 77 ° F., cm	3.5	2.5	0
P. T. S.X100 [1]	1.22	1.14	1.13

[1] Penetration temperature susceptibility = $\frac{\log 800 - \log \text{pen. at } 77\ ^\circ \text{F.}}{\text{softening point } (^\circ\text{F.}) - 77}$

As indicated by this example, asphalts obtained by the oxidation of residual oils are characterized by high temperature susceptibility. The asphalts are relatively brittle, possess poor ductility and are otherwise unsuitable for application such as the lining of irrigation canals.

EXAMPLE II

The residual oil identified in Table I was subjected to P_2O_5 treatment in the absence of air at a temperature of 450° F. Various quantities of P_2O_5, reported in weight per cent, were employed. The residual oil and P_2O_5 were stirred in a closed vessel, while passing a flow of nitrogen through the mixture to completely exclude the presence of air. The resulting asphalt possessed the following properties:

Table III.—Residual oil P_2O_5 treated in absence of oxygen

Weight Percent P_2O_5 Treat	2%	3%	4.5%
Flash Point (Cleveland Open Cup), ° F	550	535	525
Softening Point (Ring and Ball), ° F	192	225	281
Penetration at 77 ° F./100 gms./5 sec	60	55	34
Penetration at 32 ° F./200 gms./60 sec	42	36	27
Penetration at 115 ° F./50 gms./5 sec	110	90	47
Ductility at 77 ° F., cm	6	4	2.5
Penetration Temperature Susceptibility × 100	.978	.787	.673

In considering this data, it is significant that the P_2O_5 treatment in the absence of oxygen resulted in an increase in the softening point of the asphalt in proportion to the amount of P_2O_5 employed. To this extent, the treatment has a similar effect to oxidation as illustrated by Table II. However, unlike oxidation, the P_2O_5 treatment provides asphalts of lower temperature susceptibility and greater ductility at comparable softening points. This is well demonstrated by a comparison of Table II and Table III, showing the properties of three asphalts of approximately the same softening point as obtained by oxidation and P_2O_5 treatment respectively.

To further illustrate the effect of reacting P_2O_5 in the absence of air other data employing asphalts and blends of asphalts from other crude sources were obtained:

Table IV

	Vacuum Reduced Talco Crude, 110° F. S. P., 1,156 Furol Vis. Sec. at 210° F.	Talco Blend of 21/30 Pen. Straight Reduced Asphalt with Phenol Extract, 1,079 Furol Vis. sec. at 210° F.	Talco Blend of 21/30 Pen. Straight Reduced Asphalt with Phenol Extract, 836 Furol Vis. Sec. at 210° F.
Percent P_2O_5	1.2	2½	2½
Flash (Cleveland Open Cup), ° F	----------	525	530
S. P. (Ring and Ball), ° F	174	187	205
Pen., 77° F./100 gms./5 sec	47	57	53
Pen., 32° F./200gms./60 sec	29	32	31
Pen., 115° F./50 gms./5 sec	85	101	80
Duct., 77° F., cm	5¼	5½	3½
P. T. S. × 100	1.27	1.04	.92

In the data shown, the blended asphalts were prepared by utilizing the phenol extract of lubricating oil to provide asphalts of the indicated properties. These data reveal that crude source, composition, viscosity, etc., may influence, but do not prevent the reaction of P_2O_5 in the absence of air with the asphalt. The properties shown above indicate that the catalytically prepared

asphalts have lower temperature susceptibility, are more ductile and are better than those that may be produced by blending or vacuum reduction.

EXAMPLE III

As indicated, the treatment of a residual oil or an asphalt with P_2O_5 in accordance with this invention, provides asphalts having properties not obtainable by an oxidation treatment. To obtain the full benefits of this invention, therefore, P_2O_5 treatment must be conducted so as to exclude air to eliminate oxidation effects occurring simultaneously with the P_2O_5 treatment. The deleterious effects caused by the presence of oxygen while treating with P_2O_5 are shown by the following data:

Table V.—Talco flux —110° F. S. P. 1156 Furol Vis. at 210° F.

	No Air Present		Air Present	
Percent P_2O_5	0.7	1.94	0.7	1.96
S. P. (Ring and Ball), °F	130	164	127	164
Pen., 77° F./100 gms./5 sec	80	60	85	54
Pen., 32° F./200 gms./60 sec	28	30	34	27
Duct., 77° F., cm	67	10	60	5.4
P. T. S.×100	1.89	1.29	1.95	1.35

As demonstrated by this data, at the same P_2O_5 level and the same S. P. level, when reacting with P_2O_5 in the presence of air the ductility of final product is lower than when air is excluded. Also, the low temperature properties of the final product are improved when air is excluded.

EXAMPLE IV

As demonstrated, oxidation during P_2O_5 treatment is to be avoided to prevent degradation in the properties of the asphalt obtained. However, carefully controlled and relatively mild oxidation may in some cases advantageously be employed prior to the P_2O_5 treatment. This permits a reduction in the amount of P_2O_5 required to obtain an asphalt of a particular softening point, while still providing an asphalt of substantially the same quality. The asphalt obtained is superior to asphalt produced by oxidation alone or produced by P_2O_5 treatment conducted in the presence of air. This process is particularly adapted for improving the properties of an asphalt which has been oxidized.

These principles are illustrated in Table VI below, showing the effect of P_2O_5 treating an asphalt, in the absence of oxygen, after submitting the asphalt to a prior oxidation treatment conducted so as to only partially raise the softening point toward the desired value. The air blowing or oxidation treatment employed consisted of passing 30.5 cu. ft. of air/minute/ton through the asphalt for two hours at 450° F. The subsequent P_2O_5 treatment employed 1½ weight percent P_2O_5.

Table VI.—Oxidation followed by P_2O_5 treatment

	Venezuelan Flux	Air Blown	P_2O_5 Treatment of Air Blown Flux
Flash Point (Cleveland Open Cup), ° F.	485	540	540
Softening Point (Ring and Ball), ° F	90	105	198
Pen., 77° F./100 gms./5 sec	300+	173	53
Pen., 32° F./200 gms./60 sec	95	51	31
Pen., 115° F./50 gms./5 sec	300+	300+	91
Duct., 77° F., cm	--------	4.5	3.5

EXAMPLE V

It is sometimes desirable to utilize an oxidation treatment as a finishing step after a prior P_2O_5 treatment conducted in the absence of oxygen. This permits an increase in the softening point of the P_2O_5 treated asphalt without causing any substantial degradation in the other properties of the asphalt. Again this process permits obtaining an asphalt of a desired softening point and other properties while minimizing the quantity of P_2O_5 required.

Table VII shows the properties of an asphalt which was subjected to oxidation treatment after a P_2O_5 treat in the absence of oxygen. The initial feed material was a Venezuelan flux which was raised to a softening point of 232° F. by treatment with P_2O_5 in the absence of oxygen. Thereafter this asphalt was oxidized to a final softening point of 250° F. The inspections of this asphalt were as follows:

Table VII.—Oxidation of P_2O_5 treated asphalt

Flash (Cleveland open cup)_____° F__	540
Softening point (ring and ball)_____° F__	250
Penetration at 77° F./100 gms./5 sec_____	42
Penetration at 32° F./200 gms./60 sec_____	29
Penetration at 115° F./50 gms./5 sec_____	60
Ductility at 77° F., cm_____	2
P. T. S. × 100_____	0.74

The relatively high ductility and low temperature susceptibility of this high softening point asphalt are significant.

EXAMPLE VI

As brought out by the preceding examples, asphalts of desired properties are obtained by a P_2O_5 treatment in the absence of air. In particular such asphalts are noted by high softening point, low temperature susceptibility, and high ductility. However, other properties of these asphalts are notable. For example, it has been found that cut-back asphalts prepared by dilution of an asphalt with an agent such as naphtha are resistant to gellation. "Gelling" of an asphalt is notable on storage, causing a substantial increase in the viscosity of the asphalt, making use of the asphalt difficult or impossible. The gelling properties of an asphalt prepared by air blowing a Venezuelan stock and by P_2O_5 treating this stock are shown in the following table:

Table VIII

CUTBACK ASPHALT—VISCOSITY INCREASE

[45% asphalt by weight; 55% naptha by weight]

	220/235 Venezuelan Stock Prepared by air blowing; Pen. at 32° F.=11	210 S. P. Venezuelan Stock Prepared by P_2O_5 Treatment of Venezuelan Flux; Pen. at 32° F.=39
1 day	60,000+ cps.; gelled immediately	31 cps.
4 days		34 cps.
11 days		37 cps.
13 days		41 cps.
19 days		44 cps.

The P_2O_5 treated asphalt was prepared by treating the identified flux with 2.2 wt. percent of P_2O_5 with agitation in the absence of air for 5 hours at 450° F. As shown by this data, the P_2O_5 treated asphalt was not subject to gellation.

What is claimed is:

1. A process for treating residual oils comprising adding about 0.1 to 5% by weight of P_2O_5 to said residual oil and agitating said mixture in the absence of free oxygen at a temperature of about 300° to 550° F.

2. In the treatment of residual oils and asphalts with P_2O_5, the improvement which comprises adding about 0.1 to 5 weight percent of P_2O_5 to the said composition to be treated and thereafter agitating this mixture in the absence of free oxygen at a temperature of about 300° to 550° F.

3. A process for producing asphalt from a residual oil in which the residual oil is mixed with about 0.1 to 5 weight percent of P_2O_5 in the absence of free oxygen at a temperature of about 300° to 550° F.

4. The process defined by claim 3 in which the said residual oil is oxidized prior to the said treatment with P_2O_5.

5. The process defined by claim 3 in which the said treated mixture is oxidized after the said treatment with P_2O_5.

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