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ASPHALT AND PROCESS FOR MANUFACTURING SAME

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This invention concerns the treatment of residual oils and asphalts to provide improved asphaltic materials. In accordance with this invention, low molecular weight aliphatic ketones or aldehydes are employed to treat residual oils or asphalts to upgrade these materials to asphalts of desirable properties.

It is one object of this invention to provide a simple and effective manner of converting residual petroleum oils to asphalts. As used herein, the term "residual oil" 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 petroleum, from distillation of pressure tar, or from the fluxing of harder residual asphalts with heavy distillates. The residual oil may be obtained for example, from a conventional vacuum distillation zone for petroleum crude oil. Such a residual oil may be recovered as a bottoms product from such a distillation system, and is generally characterized by a specific gravity of about 0.85 to 1.07 at 77° F. Normally, such a residual oil will have a fusing point as determined by the ring and ball method falling within the range of about 32° to 120° F. It is one object of this invention to provide a novel process for the upgrading of such residual oils to asphalts having softening points above about 120° F.

The present application is also of application to the treatment of asphalts derived from other processes in order to raise the melting point of such asphalts. For example, asphalts may be obtained by the reduction of residual oils of the character identified. However, in

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hydres having about 1 to 8 carbon atoms, including formaldehyde or acetaldehyde are the preferred aldehydes. Ketones which may be employed are similarly low molecular weight aliphatic ketones having about 3 to 9 carbon atoms including acetone, methyl-ethyl ketone, methyl isopropyl ketone, methyl n-butyl ketone and diisobutyl ketone. Acetone or methyl-ethyl ketone are the preferred ketones for use in this invention.

The amount of the aldehyde or ketone to be employed in general varies from about 1% to 5% or more. For most purposes it is not necessary to employ more than 5% of the aldehyde or ketone, although quantities outside the ranges indicated may be employed if desired. A temperature above about 150° C. is required in order to secure suitable reaction of the treating re-agents with the asphaltic materials. In general, temperatures below 500° C. are to be employed. The treatment can be carried out at atmospheric pressures, although it is particularly preferred to conduct the treatment in a closed vessel permitting use of superatmospheric pressures. To some extent the time of reaction and the amount of treating agent required can be reduced by conducting the process at higher pressures.

The process does not depend upon the presence of oxygen and the benefits of this invention are to some extent obviated if oxygen is permitted to intermingle with the reactants. Although the process is preferably carried out in the substantial absence of air, it is not necessary to employ special precautions to avoid the presence of air.

The mechanism by which the ketones and aldehydes disclosed react with the asphaltic material is not presently understood.

The nature of this invention will be better understood by reference to the following data:

Example I

A residual oil of Venezuelan origin having a softening point of 116° F. was treated with 1% of acetone at a temperature of 400° C. for a period of 6 hours in a closed vessel. Air was excluded from the reaction zone and no catalyst was employed. The results of this treatment are indicated in the following table showing the properties of the original residual oil and the residual oil after treatment with the acetone.

TABLE I

	Venezuelan Residual Oil	Venezuelan Residual Oil Treated With 1% Acetone	Typical Vacuum Reduced Vene- zuelan Asphalts			Typical Air Blown Asphalts Blown from Venezuelan Residual Oil			
Softening Point (R. & B.), ° F.									
ASTM D-36-28	116	180	154	162	187	150	162	180	187
Penetration, 77°/100 g./5" ASTM D-5-49	98	18	19	12	6	22	19	14	12
Penetration, 32°/200 g./60" ASTM D-5-49	20	5	5	3½	1½	8	5	4	4
Penetration, 115°/50 g./5" ASTM D-5-49	Too Soft	49	70	43	19	80	57	38	33
Ductility, 77°, cm. ASTM D-113-44	100+	6.2	13	8½	0	16	5½	4	3½

some cases it is not practical to obtain an asphalt having a high softening point by straight reduction of a residual oil. Consequently, the process of this invention is a desirable alternative process for the upgrading of low melting point asphalts to asphalts having a high melting point.

The objectives of this invention are attained by treating the asphaltic material to be processed with a minor portion of a low molecular weight aliphatic ketone or aldehyde. The ketone or aldehyde undergoes a reaction with the asphaltic material so as to substantially change the properties of the asphaltic material. Aldehydes which may be employed are low molecular weight alde-

It will be noted from this data that the treatment with acetone was successful in substantially raising the softening point of the asphalt. The 1% of acetone employed served to raise the softening point 64° F. The final ductility of this asphalt, that is, 6.2, for an asphalt of the indicated softening point is considered unusual since the ductility is higher than that which would be obtained by air blowing or by vacuum reduction. Also at the indicated softening point the penetration at 77° F. is higher. The combination of high softening point, ductility, and penetration possessed by this asphalt qualifies the asphalt as a superior material for use in coating, laminating or saturating applications.

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Example II

In a second experiment formaldehyde was employed as the treating agent for an oxidized Venezuelan asphalt having a softening point of 244° F. This experiment was conducted to determine whether or not the softening point of this oxidized asphalt could be improved by the treatment of this invention. The formaldehyde was employed in the form of para-formaldehyde using 3% based on the weight of the asphalt. The reaction was carried out in a closed vessel for one hour at a temperature of about 160° C. The properties of the original asphalt and the treated asphalt are presented in Table II below:

TABLE II

	Air Blown Oxidized Venezuelan Asphalt	Asphalt Treated with 3% Paraform- aldehyde
Softening Point (R. & B.), °F.....	245	276
Penetration, 77°/100 g./5".....	6	5
Penetration, 32°/200 g./60".....	5	1
Penetration, 115°/50 g./5".....	10	10
Ductility, 77°, cm.....	0.9	0.4

It will be noted from the data of Table II that again the formaldehyde was successful in raising the softening point of the asphalt. This was accomplished without any substantial change in the other asphalt properties listed.

Example III

In a further experiment a residual oil having a softening point of 117° F. was treated with paraformaldehyde in a closed vessel for one hour at 150° C. A final product was obtained having a softening point of 130° F., a 77°/100/5" penetration of 50, a 32°/200/60" penetration of 15, and a 115°/50/5" penetration of 250. The ductility at 77° F. was determined to be 100+. Again it will be seen from this data that the process of this invention was effective in upgrading the residual oil to an asphalt of desirable properties. The data of this experiment is summarized in Table III.

TABLE III

	Venezuelan Residual Oil	Residual Oil Treated with 3% Paraform- aldehyde
Softening Point (R. & B.), °F.....	116	130
Penetration, 77°/100 g./5".....	98	50
Penetration, 32°/200 g./60".....	20	15
Penetration, 115°/50 g./5".....	Too Soft	250
Ductility, 77°, cm.....	100+	100+

Example IV

To establish the relationship between the softening point, penetration, and ductility properties given, and properties required in non-staining asphalt applications, tests were determined to find the stain value of asphalts as treated in the foregoing experiments. The asphalt employed in this example was a Venezuelan residual oil treated with acetone having the properties shown in Table IV. For comparative purposes, two different grades of Venezuelan oxidized asphalts were also tested for stain properties. The stain test employed was the so-called Texas Stain Test, and the procedure and equipment used is reported in Industrial and Engineering Chemistry, 42, 2340-3 (1950); Oil Exudation Properties of Asphalts, E. C. Knowles, F. C. McCoy, H. E. Schmeier, and C. E. Wilkinson. Briefly, the test consists of determining the number of cigarette papers which are stained by the oils exuding from a sample of asphalt. A high value indicates a poor asphalt. As described in the literature, the test involves placing a number of sheets of cigarette paper in contact with an asphalt surface. The paper and asphalt, in a prescribed mold, are placed in an oven for a given

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time after which the number of stained papers are recorded. The results of these experiments are indicated in Table IV.

TABLE IV

	Venezuelan Residual Oil Treated with 1% Acetone	Venezuelan 160/180 Ox- idized As- phalt	Venezuelan 220/235 Ox- idized As- phalt
Stain Value, Daylight.....	3	5½	21
Softening Point (R. & B.), ° F....	180	166 (173 Glyc)	232
Penetration, 77°/100 g./5".....	18	25	15
Penetration, 32°/200 g./60".....	5	14	9
Penetration, 115°/50 g./5".....	49	54	25
Ductility, 77°/cm.....	6.2	4.8	2.8

As shown by this data the acetone treated sample has less tendency to stain than either the 160/180 oxidized or 220/235 oxidized Colombian asphalts. The stain value of the acetone treated sample is lower than either (1) the lower softening point-higher penetration 160/180 oxidized; or (2) the higher softening point-lower penetration 220/235 oxidized asphalts. In addition the ductility of the treated asphalt is higher than either of the two asphalts.

What is claimed is:

1. A process for improving the properties of a petroleum asphaltic material in which the said asphaltic material is reacted at a temperature of at least about 150° C. with about 1 to 5% by weight of a compound selected from the group consisting of C₁ to C₈ aliphatic aldehydes and C₃ to C₉ aliphatic ketones.

2. A process for increasing the melting point of a petroleum residual oil in which the residual oil is reacted with about 1 to 5% by weight of a compound selected from the group consisting of C₁ to C₈ aliphatic aldehydes and C₃ to C₉ aliphatic ketones at a temperature above about 150° C.

3. The process defined by claim 2 in which the said reaction is conducted at superatmospheric pressures.

4. The process defined by claim 2 in which the said reaction is carried out in the absence of oxygen.

5. The process defined by claim 1 wherein said compound is formaldehyde.

6. The process defined by claim 1 wherein said compound is acetaldehyde.

7. The process defined by claim 1 wherein said compound is acetone.

8. The process defined by claim 1 wherein said compound is methylethyl ketone.

9. A process for improving the properties of a petroleum asphaltic material, including increasing the softening point thereof, in which said asphaltic material is reacted with about 1 to 5% of formaldehyde at a temperature in the range of about 150° to 500° C. in the substantial absence of oxygen.

10. The process defined by claim 9 wherein said asphaltic material is an oxidized asphalt obtained from a Venezuelan petroleum oil and has a softening point of about 244° F.

11. The process defined by claim 9 wherein said asphaltic material is a Venezuelan residual oil having a softening point of about 117° F.

12. A process for improving the properties of a petroleum asphaltic material, including increasing the softening point thereof, in which said asphaltic material is reacted with about 1 to 5% of acetone at a temperature in the range of about 150° to 500° C. in the substantial absence of oxygen.

13. The process defined by claim 12 wherein said asphaltic material is a Venezuelan residual oil having a softening point of about 117° F.

14. As a new composition of matter a petroleum derivative prepared by reacting a material selected from the group consisting of asphaltic material and residual oil with about 1% to 5% by weight of an aliphatic carbonyl

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compound having no more than 9 carbon atoms at a temperature of at least about 150° C.

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