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HEAVY-DUTY INDUSTRIAL GREASE

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12 Claims. (Cl. 196—151)

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This invention relates to new asphaltic compounds and to the method of making the same, and more particularly to the production of semi-solid materials suitable for use as lubricants on heavy bearing surfaces and gears which operate at comparatively slow speed and as a coating on surfaces to be protected from atmospheric and other corrosion agencies. The compounds are of particular utility for application on cables and moving parts of hydraulic machinery, and on metal parts exposed to the out-of-doors because of the high adhesiveness they have to metals under adverse conditions of moisture and dust, and because of their resistance to flow at elevated atmospheric temperatures. The high flash point and extreme stability to heat which certain of these products possess are highly desirable properties in lubrication of heavy industrial machinery such as rolling mills.

According to my invention the compounds are prepared by a two-step process. A residuum carefully reduced without decomposition from a crude oil to have a flash point, C. O. C., (ASTM D92–45) of at least 400° F., but preferably 475° F. or higher, is air blown at a temperature in the range of 400° F. to 550° F. in the presence of a minor amount of a catalyst or agent which promotes an increase in penetration of the product for a given softening point. The blowing is continued until the softening point (R and B), (ASTM D36–26), becomes at least 230° F. and not more than 350° F. The type of catalyst or agent and amount to employ are selected according to its action on the particular residuum to obtain a product with a needle penetration at 77° F., (ASTM D5–25), for a given softening point such that the penetration temperature susceptibility (PTS) calculated according to the relation given hereinafter will be within the range of 0.005 to 0.015.

$$PTS=\frac{\log_{10}800-\log_{10}\text{penetration at }77^\circ F.}{\text{softening point }(R\text{ and }B)\,^\circ F.-77}1.8$$

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As the second step, this air-blown asphalt is blended (fluxed back) to obtain a compound with the desired dropping point (ASTM D566–142) by addition of from 15 to 70 percent of a residuum of the type air-blown or with other residua or with a lubricating oil distillate or fraction or with a gas oil fraction, or mixtures thereof. The exact amount and choice of blending stock depends upon the characteristics desired, as will be explained hereinafter. For most purposes the dropping point is required to be above 130° F. and the unworked penetration at 77° F. as determined with the grease cone, 150 g., 5 sec., (ASTM D217–44T) in the range of 75 to 350 mm./10, but for certain applications as for greases to be used at low temperatures, products of higher penetration and lower dropping point may be desired.

It is known that products of a fairly high penetration for a given softening point can be obtained by air-oxidation of low viscosity and low flash point paraffinic residua or lube stocks. But from a given base no control is had over the body or plasticity of the product. Such asphalts are not suitable for many applications because they flow at high atmospheric temperatures and tend to be unstable and exude oils and to break down under working. In general, they are not suited for heavy duty service. Because of their high paraffinicity they show adhesion to metal surfaces and can be displaced relatively easily by water. Their weathering characteristics are poor and they cannot be recommended as protective coatings for outdoor applications.

With the aid of catalysts asphaltic products which are high in penetration for a given softening point can be air blown from most types of crude oil residua. These products, when blown from naphthenic or asphaltic residua have been found to be stable in nature. Products which are

high in flash point can be obtained by proper selection of the base and catalyst. However, this direct process also does not offer control of the body and plasticity of the products. From a given base a product will be obtained which because of its body and other properties may or may not be suitable for a particular application.

The process which is the subject of this invention has been found to be highly flexible and to permit a multitude of products of different characteristics to be prepared from a given base simply by variation of the blending stock. Fluxing with residua of the air blown type to obtain the base will produce a product which is more ductile and adhesive than a product blown directly with the aid of catalyst to the same dropping point and penetration. With addition of a lube stock to the blown base a higher penetration will be obtained for the same dropping point and a large change will be found in body, with this product relatively short and low in ductility and more oily and less adhesive. With employment of paraffinic lube stocks for fluxing extreme shortness can be obtained; in fact, the product can become granular in appearance without showing a tendency to separate into layers. With a given base and choice of the fluxing stock, besides control of the plasticity and consistency and adhesiveness, the weathering properties can be markedly influenced. Also, the product obtained has a lower ash content than if the base were directly blown with an inorganic catalyst to a given dropping point and consistency since less catalyst per unit of final product is required by the fluxing process disclosed herein. Thus there is, besides the advantage of lower ash content, a matter of economy.

Variation of the dropping point and consistency relationship of the grease also can be obtained by control of the softening point and PTS of the air-blown asphalt. Thus, a base with a high softening point and low PTS will flux back to a product of softer consistency for a given dropping point. Contrariwise a product of low softening point and high PTS will produce a more solid grease for a given dropping point.

A paraffinic type of base is not normally employed since the desired consistency for a given dropping point can be obtained by fluxing bases air-blown from naphthenic or asphaltic residua in the presence of a catalyst. Products from a paraffinic base tend to break down upon working

and in general are less stable to heat and weathering influences. Preparation from an asphaltic or naphthenic type base results in a table product with a relatively high combined sulphur content. These sulphur compounds, which are polar in nature, increase the adhesiveness of the compound to metals and are known to raise the film strength of lubricating greases. Another feature is that the air blowing of asphaltic or naphthenic compounds proceeds along a somewhat different path than does the air blowing of a paraffinic type of oil. With the latter a considerable increase in saponification number is noted, part of which is due to the formation of potentially corrosive hydroxy acids. The time required to obtain a given softening point is relatively long. A considerable content of free carbon may be formed unless the temperature is held below 450° F. Asphaltic or naphthenic types of residuum upon air-blowing increase in softening point in a relatively short time and only minor amounts of saponifiable compounds are formed. The action of the catalysts or agents in this process is apparently to cause a formation of fractions which, without causing a loss in homogeneity in the asphalt, impart a very low penetration susceptibility.

In preparation of products, except those for use at low temperatures, bases and fluxing stocks normally are selected which show a flash point, C. O. C., of at least 400° F., but preferably 475° F. or higher. The products then obtained are resistant to hardening by evaporation losses and have been found to be very stable in service, whereas products of lower flash point harden after a short period of use.

Illustrations of the type of agents which can be used are the phosphorus catalysts which are the subject of my Patent No. 2,450,756. Other catalysts are the metallic salts disclosed by Abson in Patent No. 1,782,186, and the metallic halide metal powder combinations of my Patent No. 2,421,421. Considerable variations are found in the action of these catalysts on residua dependent upon the particular crude from which they were derived. But the essential feature is that the air-blowing should be conducted to have the softening point and the PTS of the blown base within the ranges as given heretofore.

For purposes of illustration the method of preparation and properties of several compounds are shown in Table I.

TABLE I

Preparation and properties of asphaltic compounds

Example No.	Base air-blown from	Catalyst and per cent by weight	Properties of Base			Blending Stock	
			S. P. (R and B) °F.	Pen. at 77° F. (Needle), mm./10	PTS	Type	Per cent by weight
1	Smackover residuum of 25 sec. float at 122° F. and 480° F. flash C. O. C.	$ZnCl_2$, 2.0 and Cu powder, 0.5.	279	135	0.0069	Base Flux	35
2	As 1	P_2O_5, 3.0	301	123	0.0065	Heavy Naphthenic lube stock of 207 sec. S. Univ. Vis. at 210° F.	30
3	As 1	P_2O_5, 1.8	296	93	0.0077	SAE 40 Paraffinic base lube oil	40
4	As 1	P_2O_5	296	93	0.0077	Smackover Virgin Gas Oil	30
5	Schuler residuum of 20 sec. float at 122° F. and 450° F. flash, C. O. C.	P_2O_5, 3.0	248	176	0.0069	Base Flux	25
6	Schuler residuum of 32 sec. float at 122° F. and 490° F. flash C. O. C.	$FeCl_3$, 3.0	328	66	0.0078	SAE 30 Paraffinic base oil	25
7	Kerr Lynn residuum of 27 sec. float at 122° F. and 500° F. Flash, C. O. C.	FeCl, 3.0	325	59	0.0082	Base Flux	35
8	As 7	P_2O_5, 2.0	283	40	0.0114	SAE 30 Paraffinic Base lube oil	60

TABLE I

Preparation and properties of asphaltic compounds—Continued

Example No.	Base air-blown from	Catalyst and per cent by weight	Properties of Compound				Remarks
			Dropping Point, °F.	Pen. at 77° F. (Cone), mm./10	Flow,[1] 2 hrs. at 125° F., cm.	Flash Point C. O. C., °F.	
1	Smackover residuum of 25 sec. float at 122° F. and 480° F. flash C. O. C.	$ZnCl_2$, 2.0 and Cu powder, 0.5.	178	160	0.3	480	Highly homogeneous, bright surface. Ductile and highly adhesive.
2	As 1	P_2O_5, 3.0	230	154	0.0	500	Highly homogeneous, bright surface. Ductile but somewhat shorter in body than 1.
3	As 1	P_2O_5, 1.8	220	158	0.0	490	Surface somewhat dull. No tendency to separate. Medium short in body.
4	As 1	P_2O_5, 1.8	130	239	>2	230	Very fluid and workable grease at low temperature. Highly homogeneous. Medium short in body.
5	Schuler residuum of 20 sec. float at 122° F. and 450° F. flash, C. O. C.	P_2O_5, 3.0	185	162	0.2	460	Surface slightly dull. No tendency to separate. Medium short in body.
6	Schuler residuum of 32 sec. float at 122° F. and 490° F. flash C. O. C.	$FeCl_3$, 3.0	180	176	0.2	480	Slight granular appearance, very dull surface. No tendency to separate. Very short body.
7	Kerr Lynn residuum of 27 sec. float at 122° F. and 500° F. Flash, C. O. C.	FeCl, 3.0	191	132	0.2	500	Slight granular appearance, very dull surface. No tendency to separate. Short body.
8	As 7	P_2O_5, 2.0	175	200	0.0	485	Smooth appearance, dull surface. No tendency to separate. Very short body.

[1] For method of test see footnote, Table II.

Residua from three types of Arkansas crude oils which vary widely in characteristics were blown in the presence of catalysts to form bases. The well known Smackover crude oil is asphaltic in nature. Schuler crude oil is of the paraffinic-naphthenic type and distills to a residue somewhat more naphthenic than most crude oils from the mid-continent area. Kerr Lynn crude oil is highly paraffinic in nature and contains a low content of asphalt. Example No. 1 describes a product prepared from a Smackover residuum of 25 seconds float at 122° F. (ASTM D139–27). This residuum was air-blown in the presence of a zinc chloride-copper powder catalyst at a temperature of 480° F. to a softening point (R and B) of 279° F. and a needle penetration at 77° F. of 135. The PTS of this blown asphalt calculated to be 0.0069. To this blown base 35% by weight of the Smackover residuum was added to obtain a product of 178° F. dropping point and with a cone penetration of 160 mm./10 and a flash point, C. O. C., of 480° F. The flow shown at 125° F. after two hours time was 0.3 cm. The product was homogeneous with a bright black surface and was of relatively high ductility and adhesiveness. This compound is well suited as a heavy duty grease on outside gears and cables. Besides action as a lubricant, lasting protection from corrosion will also be offered because of the ability of these compounds to displace water from metal surfaces and to resist weathering action.

The product of Example No. 2 was obtained by the addition of 30% of a naphthenic lube stock derived from Smackover crude oil to a base air-blown from the Smackover residuum of No. 1, but in the presence of phosphorus anhydride as the catalyst. A compound of higher dropping point, but with about the same penetration, was obtained. This product differed from that of Example No. 1 in that it was somewhat shorter in body and showed no flow at 125° F. Application of this product can be made as a protective coating for pipe and metal structures, and as a grease under high atmospheric temperature conditions. Example No. 3 shows the product obtained by fluxing a base from a Smackover residual, blown in the presence of phosphorus anhydride, with 40% of a paraffinic base lube oil. This product tested about the same as that of Example No. 2, but was shorter in body and easier to spread and would offer less "drag" to a moving gear train or cable. The surface when disturbed showed some dullness which indicated less homogeneity than that shown by the compounds of Examples 1 and 2. Heat tests at 150° F. for five hours and storage under room conditions for two months showed no separation of oil. This product, because of its shortness, would be better suited for pressure gun application. Example No. 4 describes the preparation and properties of a grease which is suitable for low temperature application. In this case the base of Example No. 3 was fluxed with 30% of a gas oil distilled from Smackover crude. The flash point was low, which would make it unsuitable for operation at temperatures much above 100° F. At 32° F. the product was still readily workable.

The products of Examples 5 and 6 were prepared by fluxing bases blown from Schuler residuals. The Schuler base, because of its higher content of paraffinic hydrocarbons, fluxed to compounds which were shorter in body. The appearance was somewhat granular, which indicated lack of homogeneity; however, no tendency to separate on storage or when heated at 150° F. for five hours could be noted. These products would be desirable as greases where a short body was required. The grease of Example 6 would be especially desirable for application if a small resistance to drag would be of importance, because of its very short body.

The products described by Examples 7 and 8 were prepared by fluxing the air-blown residual of Kerr Lynn crude oil. Products which were stable to both heat and storage were obtained in both cases, even though the disturbed surfaces were dull and the products somewhat granular in appearance. Upon working considerable loss in structure and decrease in flow resistance was noted. The shortness of body would be an ad-

vantage in certain applications. These products would not have sufficient weather resistance to be recommended for application as outdoor protective coatings.

As an example of the preparation of a product suitable for application as a protective coating or as a heavy duty grease on a commercial scale, the following example is cited:

One hundred barrels of asphaltic residuum steam and vacuum reduced from Smackover crude oil and showing a float time at 122° F. of 23 seconds and a flash point, C. O. C., of 475° F. was charged to a blowing still. Six hundred pounds of phosphorus pentoxide were added to the flux charge and the mixture air-blown at a temperature of around 460° F. An asphalt with plastic-like properties and a softening point of 296° F., (R and B) and a needle penetration at 77° F. of 93 was obtained after 15 hours of air-blowing. The PTS of this product calculated to be 0.0072.

This plastic asphalt was fluxed with Smackover residuum of 23 seconds float time at 122° F. and 475° F. flash point. The addition of 21 percent of the flux by weight produced a compound with properties as shown under Example No. 1 of Table II. A portion of this product was barreled for use as a grease and as a protective coating for outdoor applications. To the remainder, additional flux was added to have a content of 37 percent to obtain the product of Example No. 2, a heavy duty gear lubricant.

TABLE II

Properties of heavy duty greases

Example No.	1	2
Dropping Point, °F.	250	185
Penetration at 77° F., 150 g., 5 sec. (Grease Cone), mm./10[1]	94	193
Flow at 125° F., 2 hrs. cm.	0.0	0.5

[1] Flow test procedure: A portion of the sample was poured to a uniform depth of 0.32 cm. into a suitable amalgamated mold 4 cm. wide by 6 cm. long, placed on a bright tin panel. After cooling at room temperature for two hours, the mold was removed and the panel containing the sample placed in an oven maintained at 125° F. During the test the panel was mounted at an angle of 75 degrees with the horizontal. After two hours had elapsed the total movement in cms. of the specimen was reported as the flow.

The grease of Example No. 2 was found easy of application and still possessed a dropping point of 185° F. and was resistant to flow under normal atmospheric temperatures.

The invention has been described in detail for the purpose of illustration, but numerous modifications and variations may be resorted to without departing from the spirit of the invention.

I claim:

1. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

2. A lubricating grease consisting essentially of a blend of an air-blown asphalt product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, said agent comprising a phosphorus containing catalyst, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

3. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, said agent comprising a metal salt, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

4. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, said agent comprising a metal halide-powdered metal combination, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

5. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, said base petroleum residuum being a non-paraffinic residuum, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

6. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of at least 400° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° F. to 350° F. and a PTS within the range of 0.005 to 0.015.

7. A lubricating grease consisting essentially of a blend of an air-blown asphalt product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of at least 475° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS from 0.005 to 0.010.

8. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetra-

tion-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS from 0.005 to 0.010.

9. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015, the blended lubricating grease having a dropping point above 130° F.

10. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a naphthenic base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

11. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from an asphaltic base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

12. A lubricating grease consisting essentially of a blend of an air-blown asphaltic product with from 15 to 70 percent of a petroleum fraction having at least the boiling point of gas oil, said asphaltic product being air-blown from a semi-asphaltic base petroleum residuum of greater than 375° F. flash point in the presence of a small quantity of a catalytic agent which acts to lower the penetration-temperature susceptibility, the air-blown base having a softening point within the range of 230° to 350° F. and a PTS within the range of 0.005 to 0.015.

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Certificate of Correction

Patent No. 2,488,293 November 15, 1949

ARNOLD J. HOIBERG

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 31, after the word "show" insert *low*; column 4, line 4, for "table" read *stable*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of April, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.