

## UNITED STATES PATENT OFFICE

2,055,043

## MANUFACTURE OF LUBRICANTS

Roy F. Nelson, Nederland, Tex., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application September 28, 1932,  
Serial No. 635,226

13 Claims. (Cl. 87-9)

This invention relates to the manufacture of lubricants comprising certain hydrocarbons which have been subjected to a regulated degree of oxidation.

5 Lubricants of any desired hardness and melting point have been prepared according to the U. S. patent to Dengler No. 1,781,444, dated November 11, 1930, by subjecting a paraffin or semi-paraffin base crude petroleum to distillation  
10 under such conditions that decomposition or cracking does not take place to an appreciable degree, continuing the distillation until the residue has the desired properties as determined by proper tests, then subjecting the residue to an  
15 oxidizing treatment at elevated temperature, the temperature and the amount of oxidation being carefully controlled to produce the desired properties, which will depend upon the use to which the final product is put.

20 Lubricants of this type are of excellent body and are well suited for use under conditions of very high pressure and comparatively slow speed where a lubricant having considerable body is required to separate the bearing surfaces. They  
25 are also very highly resistant to decomposition from heat. A further advantage in the use of such lubricants is that they have a certain adhesiveness which aids the lubricant to adhere to the bearing surfaces.

30 It is characteristic of such lubricants that in the higher melting point grades they are of very sticky texture and do not have the lubricating quality which is desired of some lubricants. It is an object of the invention to provide a series of  
35 lubricants of this class which are of smooth oily texture and which are less sticky than the oxidized residues from which they may be prepared.

A further characteristic of lubricants prepared from oxidized residues is that they set upon initial cooling to form products which appear to  
40 be of a certain hardness but which after a brief period of stirring or working may become relatively soft. It is also observed that these lubricants tend to flow upon standing at comparatively  
45 low temperatures. The invention contemplates a series of lubricants of improved consistency in which these conditions do not obtain.

The texture of these lubricants may be improved by blending therewith a petroleum oil having the desired oiliness or lubricating quality,  
50 however, the addition of the oil tends to soften the product and to lower its melting point so that lubricants of suitable texture having the  
55 desired hardness and melting point are difficult to obtain.

I have discovered that upon oxidation, certain petroleum residues may contain a substantial amount of matter which is readily saponified  
60 with an alkali to form soap. The formation of

soap in the residue tends to increase the hardness thereof and to raise its melting point.

The invention contemplates converting the contained saponifiable matter in an oxidized residue to soap to thereby increase the hardness of  
5 the residue and to raise its melting point and further contemplates blending with the residue a petroleum oil to improve the oiliness or lubricating quality of the product. Smooth oily  
10 lubricants may thus be prepared of any desired hardness and melting point.

It is an object of the invention to produce a series of high class lubricants which are inexpensive to manufacture and which because of their excellent body and superior lubricating  
15 quality are especially suitable for use as axle grease, hot roll neck grease, etc., where conditions of high pressure and slow speed are commonly encountered.

The invention will be better understood from a  
20 consideration of the following examples which are given for the purpose of illustration and are not intended to impose any limitation upon the scope thereof.

As shown in the patent of Dengler above referred to, a crude petroleum of the type usually  
25 obtained in the Mid-Continent field, may be charged into a suitable crude still and subjected to distillation under vacuum or in the presence of steam to avoid cracking or decomposition.  
30 The distillation may be continued until the residuum has the desired properties. The residuum may then be transferred to another vessel which may be insulated or heated and air may be forced therethru to produce the desired degree of oxidation.  
35

The degree to which the original crude petroleum is reduced by distillation will affect the properties of the final product obtained. In  
40 general, it will be desirable to reduce the crude until the residuum has a flash test of from 375° to 475° F., and it may be said that oxidized lubricants prepared from low flash residuum will, for a given melting point, have a higher penetration,  
45 that is, will be softer and more nearly plastic than lubricants prepared from high flash residuum. The melting point in the final product will be dependent upon the degree of oxidation employed, long continued treatment yielding a higher melting  
50 product than a comparatively short treatment, and it is also true that the temperature at which the oxidation is carried on may have some effect upon the melting point of the final product. The temperatures of oxidation may range from  
55 about 400° F. to 515° F. but best results are usually obtained by carrying on the oxidation in the neighborhood of 450° F., as it is found that the reaction proceeds quite slowly at the lower temperatures while at the upper limits, over 500° F.,  
60

there is a tendency to form free carbon in the product.

By suitable determination it may be ascertained that the oxidized residue from the above treatment contains fatty matter which will react with a definite amount of an alkali to form soap.

In one form of my invention an oxidized residue may be processed to convert the contained saponifiable matter to soap and then blended with a suitable amount of a petroleum oil to produce a smooth oily lubricant having the desired hardness and melting point.

In carrying out the process of the invention an oxidized residue may be used having, for example, the following tests:

|                                                         |         |
|---------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) .....  | 158     |
| Melting point (dropping pt.) .....                      | 274° F. |
| Saponification value (A. S. T. M. method D94—21T) ..... | 14.9    |

In the example given .0149 parts by weight of potassium hydroxide may be required to react with the saponifiable matter contained in one part by weight of the sample. By calculation the equivalent amount of other alkalis, for example calcium or sodium hydroxide, may be determined.

The residue may be placed in a suitable kettle and subjected to heating while stirring. A quantity of lime, which may be in excess of the amount required to react with the contained saponifiable matter, may be mixed with the residue in the form of a thick slurry or suspension in water.

The percentage of ingredients may be about as follows:

|                                               | Percent |
|-----------------------------------------------|---------|
| Oxidized residue .....                        | 89.36   |
| Lime (98.81% $\text{Ca}(\text{OH})_2$ ) ..... | 2.51    |
| Water .....                                   | 8.13    |
|                                               | 100.00  |

The mixture may be continuously heated while stirring for a sufficient period of time to effect saponification of the contained saponifiable matter. During the heating the residue may be partially dehydrated, although a small amount of water is preferably retained in order to make a smooth less sticky product. A petroleum oil which may be of the order of 100 viscosity may be blended with the residue to produce a finished lubricant of smooth oily texture and having the desired hardness and melting point which may be regulated by the amount of oil so added.

A finished lubricant prepared in the above manner and containing, say 4.54% of petroleum oil on the basis of the oxidized residue, may have the following tests:

|                                                        |         |
|--------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) ..... | 137     |
| Melting point (dropping pt.) .....                     | 137° F. |
| Water .....                                            | 5.8%    |
| Calcium soap .....                                     | 11.4%   |
| Uncombined lime .....                                  | 1.63%   |

It will be observed that although the finished lubricant contains more than 10% of petroleum oil and water, and the texture of the lubricant is thereby improved, it is of lower penetration, or harder, than the oxidized residue from which it is made. This is attributed to the presence of calcium soap.

Saponification of the saponifiable matter in an oxidized residue tends to increase the hardness thereof and to raise its melting point. A sample

of the same residue as employed in the foregoing example, also saponified by use of an excess of lime and containing no petroleum oil and only 2.5% of water, may have the following tests:

|                                                        |         |
|--------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) ..... | 103     |
| Melting point (dropping pt.) .....                     | 454° F. |

An additional sample may be saponified using 3.68% by weight of a 49% sodium hydroxide solution, on the basis of the oxidized residue. This product, containing no petroleum oil and substantially dehydrated, may have the following tests:

|                                                        |         |
|--------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) ..... | 76      |
| Melting point (dropping pt.) .....                     | 473° F. |

In a modified form of my invention an oxidized residue may be first blended with a suitable amount of a petroleum oil and the mixture then processed to saponify the saponifiable matter contained in the residue.

In carrying out the invention in its modified form a residue may be used having approximately the following tests:

|                                                         |         |
|---------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) .....  | 62      |
| Melting point (dropping pt.) .....                      | 243° F. |
| Saponification value (A. S. T. M. method D94—21T) ..... | 18.7    |

A petroleum oil which may be of the order of 100 viscosity may be blended, in a kettle provided for the purpose, with the oxidized residue. A quantity of lime, which may be in excess of the amount required to react with the saponifiable matter contained in the residue, may be mixed therewith in the form of a thick slurry or suspension in water. The percentage of ingredients may be about as follows:

|                                               | Per cent |
|-----------------------------------------------|----------|
| Oxidized residue .....                        | 75.6     |
| Petroleum oil .....                           | 20.0     |
| Lime (98.81% $\text{Ca}(\text{OH})_2$ ) ..... | 2.2      |
| Water .....                                   | 2.2      |
|                                               | 100.0    |

The mixture may be continuously heated while stirring for a sufficient period of time to effect saponification, during which time it may be substantially dehydrated. A small amount of water, for example 2%, may be added to improve the texture of the finished product.

A finished lubricant prepared in the above manner may have the following tests:

|                                                        |         |
|--------------------------------------------------------|---------|
| Penetration 77° F. (A. S. T. M. method D217—27T) ..... | 130     |
| Melting point (dropping pt.) .....                     | 248° F. |
| Water .....                                            | 1.8%    |
| Calcium soap .....                                     | 9.5%    |
| Uncombined lime .....                                  | .83     |

It will be noticed that the finished lubricant, which contains nearly 22% of petroleum oil and water, is of slightly higher melting point than the oxidized residue, which is due to the presence of calcium soap.

A sample of the same residue as employed in the foregoing example, also saponified with an excess of lime and containing no petroleum oil and substantially dehydrated, may have the following tests:

Penetration 77° F. (A. S. T. M. method  
D217—27T) ----- 52  
Melting point (dropping pt.) ----- 353° F.

It is to be understood that the term "paraffin base crude" as employed in the appended claims is intended to include semi-paraffin base crudes such as found in the Mid-Continent fields. Melting points referred to herein were taken by the method described on pages 105-107 of the article entitled "Lubrication and lubricants" by G. R. Roland, Journal of the American Society of Naval Engineers, vol. 31, 1919. This method or slight modifications thereof has been widely used with success for many years by grease chemists, and is frequently referred to as the "drop point method".

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of preparing a grease consisting essentially of a mixture of hydrocarbon oil and a soap, which comprises reducing a paraffin base crude to a residuum by distillation without substantial decomposition, blowing the residuum with air at an elevated temperature to effect oxidation and produce a substantial content of saponifiable material, and heating the oxidized residuum with an aqueous alkaline material to saponify the saponifiable content and produce a resulting grease as a uniform mixture of soap and oxidized residuum.

2. The method of preparing a grease consisting essentially of a mixture of hydrocarbon oil and a soap, which comprises reducing a paraffin base crude to a residuum by distillation without substantial decomposition, blowing the residuum with air at an elevated temperature to effect oxidation and produce a substantial content of saponifiable material, mixing a lubricating oil with the oxidized residuum, and heating the oxidized residuum mixture with an aqueous alkaline material to saponify the saponifiable content and produce a resulting grease as a uniform mixture of soap, oxidized residuum and lubricating oil.

3. The method of preparing a grease consisting essentially of a mixture of hydrocarbon oil and a soap, which comprises reducing a paraffin base crude to a residuum by distillation without substantial decomposition, blowing the residuum with air at an elevated temperature to effect oxidation and produce a substantial content of saponifiable material, and heating the oxidized residuum with lime to saponify the saponifiable content and produce a resulting grease as a uniform mixture of soap and oxidized residuum.

4. The method of preparing a grease consisting essentially of a mixture of hydrocarbon oil and a soap, which comprises reducing a paraffin base crude to a residuum by distillation without substantial decomposition, blowing the residuum with air at an elevated temperature to effect oxidation and produce a substantial content of saponifiable material, and heating the oxidized residuum with caustic soda to saponify the saponifiable content and produce a resulting grease as a uniform mixture of soap and oxidized residuum.

5. A lubricating grease consisting essentially of a substantially uniform mixture of a lubricating oil with the product resulting from the saponi-

fication of air blown residuum from paraffin base crude with an alkaline saponifying reagent.

6. A lubricating grease consisting essentially of a substantially uniform mixture of a lubricating oil with the product resulting from the saponification of air blown residuum from paraffin base crude with lime.

7. A lubricating grease consisting essentially of a substantially uniform mixture of a lubricating oil with the product resulting from the saponification of air blown residuum from paraffin base crude with caustic soda.

8. The process of preparing lubricants which comprises reducing a paraffin base crude petroleum by distillation without substantial decomposition until the residuum has a flash test within the range of 375° to 475° F., blowing the residuum with an oxidizing gas at temperatures between 400° and 515° F. to effect oxidation and produce a substantial content of saponifiable material, and then heating the oxidized residuum with an aqueous alkaline material to saponify the saponifiable content and produce a resulting lubricant as a uniform mixture of soap and oxidized residuum.

9. The process of preparing a grease which comprises reducing paraffin base crude petroleum by distillation without substantial decomposition until the residuum has a flash test within the range of 375° to 475° F., blowing the residuum with air at temperatures between 400° and 515° F. to effect oxidation and produce a substantial content of saponifiable material, and heating the oxidized residuum with an aqueous alkaline material to saponify the saponifiable content and blending with a lubricating oil to produce a resulting grease of smooth oily texture as a uniform mixture of soap, oxidized residuum and lubricating oil.

10. A lubricating grease consisting essentially of an air blown and then saponified residuum from paraffin base crude petroleum blended with a lubricating oil.

11. A lubricating grease comprising as essential ingredients a substantially uniform mixture of the unsaponifiable content of a reaction product of air oxidation at temperatures between 400° and 515° F. of a substantially undecomposed residuum from a paraffin base crude petroleum reduced to a flash test of 375° to 475° F., together with the soap formed by saponification of the saponifiable content of the said oxidation reaction product.

12. The method of preparing a grease which comprises air blowing at elevated temperatures a heavy paraffin base residual oil to effect oxidation and produce a substantial content of saponifiable material, and then heating the oxidized residuum with an alkaline material to form soap by saponification of saponifiable material in the oxidized residuum.

13. The method of preparing a grease which comprises air blowing at elevated temperatures a heavy paraffin base residual oil to effect oxidation and produce a substantial content of saponifiable material, and then heating the oxidized residuum with an alkaline material to form soap by saponification of saponifiable material in the oxidized residuum and blending with a lubricating oil to produce a resulting grease of smooth oily texture.

ROY F. NELSON.