

1

3,392,119
GREASE

Bill Mitacek, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware
No Drawing. Filed Oct. 11, 1965, Ser. No. 494,897
3 Claims. (Cl. 252-59)

ABSTRACT OF THE DISCLOSURE

Grease is formed from a white mineral oil, polypropylene, and a polymer of ethylene.

This invention relates to a method for making an improved grease and the product thereof.

Heretofore some greases have been formed by adding to a conventional lubricating oil base, for example, mineral, vegetable or animal oils and mixtures thereof, a polymer as a thickening agent. In the past specific, single polymers have been employed in lubricating oils in general.

Quite surprisingly, it has now been found that a grease having certain improved properties is formed when white mineral oil is thickened by the use of certain polymers of ethylene, as hereinafter defined, and a homopolymer of propylene. It was unexpectedly found that not only do white oils respond differently to such polyolefin thickening than do conventional lube oils but the blending of white oils with a polymer of ethylene and a polymer of propylene results in greases having improved non-bleeding characteristics.

Accordingly, the improved grease of this invention comprises a major amount of white mineral oil and a minor amount of at least two polymers, one being a polymer of ethylene as hereinafter defined and the other being a homopolymer of propylene.

An object of this invention is to provide a new and improved method for making a grease. Another object of this invention is to provide a new and improved grease.

Other aspects, objects and the several advantages of this invention will be readily apparent to those skilled in the art from the description and the appended claims.

According to this invention an improved grease is prepared by thickening white mineral oil with individual polymers of both ethylene and propylene. It has also been found that the improvements in the grease of this invention are not realized when only one of the two polymers is employed or when oils other than white mineral oil are used.

The white mineral oils of this invention are colorless white oils consisting essentially of saturated aliphatic hydrocarbons and are substantially free of aromatics and other unsaturated compounds. White oils are well known in the art and are produced by refining lubricating oil fractions, for example by solvent extracting a lubricating oil and then treating the extracted portions with oleum. Generally, the white oils of this invention have a Saybolt viscosity of from about 40 to about 150 SUS at 210° F. and a pour point (ASTM D97-57) at least as low as about 40° F. and preferably below about 10° F. Depending upon the grade of the white oil employed, the greases of this invention can be used for conventional purposes including use with or in close proximity to food and its preparation.

The ethylene polymers used in this invention have a density at 25° C. of at least 0.94 gram per cubic centimeter. The density of these polymers generally will not exceed 0.97 although more dense polymers, e.g. up to 1.00, are possible and can be used in this invention. In this discussion, these ethylene polymers are referred to as "high density" polymers while the term "low density" is

2

reserved for those ethylene polymers having a density below 0.94.

In a preferred density determination method, the specimens should be prepared by compression molding the polymer at 340° F. until completely molten followed by cooling to 200° F. at a rate of about 10° F. per minute. Water is then circulated through the mold jacket to continue the cooling to 150° F. at a rate not exceeding 20° F. per minute. The polymer is then removed from the mold and cooled to room temperature.

Density is determined by placing a smooth, void-free, pea-sized specimen cut from a compression molded slab of the polymer in a 50 ml., glass-stoppered graduate. Carbon tetrachloride and methylcyclohexane are added to the graduate from burettes in proportion such that the specimen is suspended in the solution. During the addition of the liquids the graduate is shaken to secure thorough mixing. When the mixture just suspends the specimen, a portion of the liquid is transferred to a small test tube and placed on the platform of a Westphal balance and the glass bob lowered therein. With the temperature shown by the thermometer in the bob in the range 73-78° F., the balance is adjusted until the pointer is at zero. The value shown in the scale is taken as the specific gravity. With the balance standardized to read 1.000 with a sample of distilled water at 4° C. the specific gravity will be numerically equal to density in grams per cc.

Of course, other procedures which produce equivalent results can be used.

The ethylene polymers employed in this invention can include copolymers although homopolymers are presently preferred. Copolymers can be formed of ethylene with at least one other olefin of higher molecular weight, e.g. up to 8 carbon atoms per molecule, preferably containing no branching nearer the double bond than the 4-position. Examples of suitable comonomers include propylene, 1-butene, 2-butene, 1-pentene, 1-octene, 4-methyl-1-pentene, 4-ethyl-1-pentene, 4-methyl-1-hexene, 6-methyl-1-heptene, 4-ethyl-1-hexene, and the like. Preferred copolymers include ethylene with propylene or 1-butene. In general, ethylene makes up at least 95 weight percent of the copolymer. In forming such a polymer the monomer feed to the polymerization zone will ordinarily be at least 80 percent by weight ethylene. As the percent of ethylene in the copolymer is decreased the density of the polymer likewise is decreased so that the density limitation can be used as an indication of copolymer composition. In other words, if the density of the copolymer is 0.940 or above, it will be suitable for my invention.

Methods of preparing the ethylene polymers of high density are now well known. A preferred method is described in the United States Patent 2,825,721, which issued March 4, 1958, to J. P. Hogan et al. Suitable polymers can be prepared in other low pressure processes, for example, processes which employ what are commercially known as organometal catalyst systems.

The homopolymers of polypropylene which are employed in this invention have a density at 25° C. of between 0.890 and 0.920 gram per cubic centimeter. The density of the polypropylene is determined in the same manner as set forth hereinabove with respect to the ethylene polymers. The melt index of the propylene polymers can vary widely, for example from about 0.1 to 25, but preferably has a melt index of from 1 to 6 as determined by ASTM D1238-62T, Procedure E.

The amount of combined polymers of ethylene and propylene in the grease of this invention can vary widely but will generally be from about 2 to about 15 weight percent total polymeric thickeners based upon the total weight of the grease. The weight ratio of polyethylene to polypropylene will generally be in the range of from about 10:1 to about 1:10, preferably 3:1 to about 1:2.

The grease of this invention can be prepared in a conventional manner such as by heating the white oil, adding the polymers together or sequentially to the heated oil, stirring the oil and polymer mixture and, if desired, thereafter milling the mixture in a colloid mill or other high-speed apparatus which produces severe agitation and substantial shearing in the mixture. The white oil can be initially heated to a temperature in the range of from about 325 to about 450° F. after which the polymers can be added in solid form in the size of conventional pellets or in a more finely divided state if desired. Thereafter adequate dispersion can generally be obtained by agitating the heated mixture for one to sixty minutes. If desired, milling can then be carried out at a temperature in the range of from about 150 to about 245° F., preferably 180 to 200° F. For additional details on grease milling see "Manufacture and Application of Lubricating Greases," chapter 5, Reinhold Publishing Corporation, New York (1954).

After milling the grease can be cooled to ambient temperatures for use or storage, as desired.

The grease of this invention can contain other conventional additives and modifiers such as antioxidants, rust inhibitors, fillers, pigments, and the like. Some examples of such materials include propylenediamine, phenyl- α -naphthylamine, phenothiazine, mica, asbestos, powdered lead, powdered zinc, talc, alumina, titanium dioxide, molybdenum disulfide, bentones, carbon black, nitrobenzene and the like. Generally, the amount of these modifiers is less than about 10 percent of the total weight of the grease.

EXAMPLE I

A "pure food" grease was prepared from a white mineral oil having a viscosity of 52.83 SUS at 210° F. thickened with both a homopolymer of ethylene having a density at 25° C. of 0.96 gram per cubic centimeter and a melt index of 5 (ASTM D1238-62T, Procedure E) and a homopolymer of propylene having a melt index of 4 (ASTM D1238-62T, Procedure E), a flexural modulus of 213,000 p.s.i. (ASTM D790-61), xylene solubles of 5.3 weight percent, and 92 p.p.m. ash.

To prepare the grease, 89 weight parts of the white oil were charged to a cast-iron pressure kettle, which was jacketed for circulation of hot oil, together with 6.5 weight parts of the polyethylene. The contents of the kettle were heated to about 325° F. and the mixture was agitated by circulation from the bottom of the kettle to spray heads at the top of same. The polypropylene (4.5 weight parts) was then added and the kettle contents heated to 375 to 380° F. Heating was then stopped and the heated mixture pumped through a scraped surface heat exchanger (Votator) to lower the temperature to 160° F. The resulting grease was then milled in a Charlotte colloid mill under conditions such that the temperature of the grease issuing from the mill was in the range of 180 to 200° F. Entrained air was removed from the hot grease with a vacuum pump.

For purposes of comparison the same grease preparation procedure was repeated twice more; once with the white mineral oil being thickened with a similar quantity of polyethylene only; and once with the white mineral oil being thickened with a similar quantity of polypropylene only. The three greases obtained were then tested and the results are as follows:

Table I

White Mineral Oil Thickened with—	Wheel Bearing Leakage, g. (ASTM D1263-53T)	Bleed Test, 24 Hrs. Wt. percent (ASTM D1742-60T)
Polyethylene, 10 wt. percent ¹	16.5	11.1
Polypropylene, 12 wt. percent.....	23.4	8.4
Polyethylene, 6.5 wt. percent.....	8.5	4.6
Polypropylene, 4.5 wt. percent.....		

¹ Weight percent above and in following tables based on total weight of grease.

From the above data it can be seen that white mineral oil thickened with both polyethylene and polypropylene exhibits substantial improvement in both the wheel bearing leakage test and the bleed test over similar greases formed using only one of polyethylene or polypropylene as the thickener.

The above grease preparation procedure was again repeated, only this time instead of a white oil, a conventional naphthenic lubricating oil stock which was not oleum treated and therefore contained substantial amounts of aromatic and other unsaturated organic compounds was used. The particular naphthenic oil employed was a combination of 64 weight percent "Necton 78" and 36 weight percent "Necton 37". The "Nectons" are solvent refined naphthenic oils sold by Humble Oil Company.

The grease obtained using the naphthenic oil in lieu of the white mineral oil was then tested and the results are as follows:

Table II

Bleed test (ASTM D1742-60T), 24 hrs., wt. percent

Naphthenic oil thickened with:	
Polyethylene, 11 wt. percent	10.6
Polypropylene, 11 wt. percent	13.5
Polyethylene, 6.5 wt. percent }	11.0
Polypropylene, 4.5 wt. percent }	

These tests showed that the combination of polymeric thickening agents when employed in a naphthenic oil offered no improvement over the individual thickening agents in the naphthenic oil.

To further show that the improvement of this invention is obtained with white mineral oil and not with other oils, the grease preparation procedure and formulation employed for the naphthenic oil was repeated with white mineral oil having a viscosity of 52.83 SUS at 210° F. The grease obtained was then tested and the results are as follows:

Table III

White mineral oil thickened with:	
Bleed test (ASTM D 1742-60T),	
	24 hrs., wt. percent
Polyethylene, 11 wt. percent	19.4
Polypropylene, 11 wt. percent	9.2
Polyethylene, 6.5 wt. percent }	5.4
Polypropylene, 4.5 wt. percent }	

These tests show the unexpected improvement in the bleed test for the combination of polyolefin thickeners which was not predictable from the tests using the individual polyolefin thickeners.

From the data of Tables II and III it can be seen that the improvement of this invention is not obtained with oils containing substantial amounts of aromatics and other unsaturated organic compounds.

Reasonable variations, and modifications, are possible within the scope of this disclosure without departing from the spirit and scope thereof.

I claim:

1. A grease of improved properties comprising a major amount of white mineral oil and a minor thickening amount of a homopolymer of propylene and at least one polymer of ethylene selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one olefin of higher molecular weight up to 8 carbon atoms per molecule, said copolymers containing not more than 5 weight percent of said higher molecular weight olefins, the combined amounts of said polymers being effective to obtain the improved properties.

2. The grease of claim 1 wherein said white oil consists essentially of saturated aliphatic hydrocarbons and the combined polymers of ethylene and propylene are present in the amount of from about 2 to about 15 weight percent based on the total weight of the grease, the weight ratio of the polymer of ethylene to the polymer of pro-

5

pylene being in the range of from about 10:1 to about 1:10, and the polymer of ethylene has a density of at least 0.94 grams per cubic centimeter at 25° C.

3. A grease of improved physical properties comprising a major amount of white oil having a Saybolt viscosity of from about 40 to about 150 SUS at 210° F. and a pour point at least as low as 40° F. as determined by ASTM D97-57, and a minor thickening amount of individual homopolymers of ethylene and propylene, the weight ratio of the polyethylene to the polypropylene being in the range of from about 10:1 to about 1:10, the combined amount of said homopolymers being effective to obtain the improved properties, and the polymer of

6

ethylene has a density of at least 0.94 grams per cubic centimeter at 25° C.

References Cited

UNITED STATES PATENTS

2,791,576	5/1957	Field et al.	252—59
2,810,695	10/1957	Young et al.	252—59
3,076,764	2/1963	Hansen et al.	252—59
3,112,270	11/1963	Mitacek et al.	252—59
3,169,114	2/1965	Mitacek et al.	252—59

DANIEL E. WYMAN, *Primary Examiner.*

I. VAUGHN, *Assistant Examiner.*