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POUR DEPRESSANTS

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The present invention relates to improved pour point depressants for lubricating oils and the like. It relates more generally to improvements in the art of producing wax modifying agents, particularly those which may be employed for reducing the pour point of waxy lubricating oils, especially mineral base oils, or in connection with processes for dewaxing oils containing paraffinic wax. The invention may have application in other processes or compositions in which a wax structure is to be modified by reducing the crystal size.

In U. S. Patent 2,251,550, granted to Lieber, there is described a process of producing an effective wax modifying agent by heat condensation-polymerization of the acid chloride which is derived from fatty acids containing 10 to 20 carbon atoms. The product described in said patent has been found highly effective for its purpose, having a pour point ceiling of slightly below -30° F. Although this is an excellent showing, it has been even further improved upon by the present invention which reduces the pour point of waxy mineral oils to -35° F. by ASTM test and at the same time is pour stable to -22° F. by the S. O. D. Pour Stability Test. This test is described in detail in Transactions of American Society of Automotive Engineers, vol. II, No. 1, pp. 34-44. The latter feature is of considerable importance.

According to the present invention, satisfactory wax modifying agents may be prepared by the direct pyrolysis of mixtures of two or more fatty acid halides. The chlorides are specifically preferred but the other halides, and especially the bromides, are quite useful. For this purpose, aliphatic carboxylic acid halides containing from 10 to 30 carbon atoms per molecule, the range of 12 to 22 carbon atoms being more generally preferred, are heated to a temperature of 400° to 800° F., preferably 500° to 700° F., for a period of 1 to 10 hours, preferably from 2 to 5 hours. While normal atmospheric pressure may be used, reduced pressures are often advantageous in carrying out this process. The resulting product may be refined in various ways, such as filtration or distillation, to remove raw materials in low boiling condensation products or by solvent extraction, clay-treating, and the like.

The exact nature of the chemical process involved is not known, but it is believed that the process is primarily a dehydrohalogenation-condensation reaction.

The aliphatic acid halides employed, the chlorides for example, in the process of the present invention may be straight or branched chain com-

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pounds, saturated or unsaturated, and may be monobasic or polybasic. Preferably at least one monobasic acyl halide is combined with at least one dibasic acyl halide. Examples of the preferred acids include stearic acid, palmitic acid, margaric acid, lauric acid, oleic acid, sebacic acid, coconut oil acids, wax oxidation acids, and the like. The following description relates mainly to the chlorides but is applicable to the other halides.

The hydrocarbon base stocks into which the wax modifying agents of the present invention are incorporated are preferably waxy mineral base lubricating oils such as a paraffinic lubricating oil base stock or a mixed base, which may have been subjected to any one or more of the commonly used refining steps, such as distillation, solvent extraction, acid treating, clay treating, etc., as well as partial dewaxing. Such oil base stock may either be one which is within the known lubricating oil viscosity range or it may be an oil of much lower viscosity, such as a gas oil used in the preparation of hydraulic oils, etc., and which may have a viscosity as low as 40 Saybolt seconds at 100° F. Solid or normally solid hydrocarbon base stocks may be used, such as the paraffin waxes of the type employed for hot melt coating of paper.

In carrying out the invention, it is desirable to use the wax modifying additive in proportions of about 0.1 to 5% based on the weight of lubricating oil base stock, although usually about 1% is sufficient for most purposes. Proportions of 0.5 to 2% are specifically preferred. It will be understood that different oils require slightly different amounts of the material to produce a given drop in pour point, and likewise material prepared from different types of acids vary somewhat in their pour depressing strength.

The wax modifying agents of the present invention may be used in connection with the process for dewaxing hydrocarbon oils. They may be added either to the oil to be dewaxed or to the oil after it has been diluted with naphtha or with other suitable dewaxing solvents. The mixture containing the wax is chilled to the wax separating point and the actual separation may be conducted either by filtration, sedimentation or centrifugation. In any case, it will be found that the presence of a relatively small amount of the wax modifying material, say 1% more or less, will considerably increase the ease with which the wax separation is accomplished and increase the rate at which chilling may be carried out.

The compounds described herein may be combined with other lubricating oil additive materials such as dyes, antioxidants, pour depressants, thickeners, viscosity index improvers, metallic soaps, extreme pressure agents, and the like.

The desirable results obtained by the use of the additives described in the present specification may be illustrated by the following example which, however, is not to be considered as limiting the scope of the invention in any way.

Example

A mixture of one part by weight of sebacyl chloride (20 g.) and nine parts by weight of stearoyl chloride (180 g.) were heated to 260° C. during a period of ½ hour and held at this temperature, $\pm 5^\circ$ C. for 3 hours. Considerable quantities of hydrogen chloride were evolved. The final dark waxy product (169 g.) was tested and found to be free of chlorine. A portion of this material was blended in a base oil of about 44 S. U. S. viscosity at 210° F., consisting essentially of a solvent extracted Mid-Continent neutral oil plus 3½% conventionally refined Pennsylvania Bright Stock and the pour points of the blends were determined.

Pour point of blends, ° F.

0%	¼%	½%	¾%	1%
+30	+10	-10	-20	-35

The pour stability of the 1% blend of the pyrolysis product of the mixed acid chlorides, as determined in the S. O. D. Pour Stability Test, as described above, was found to be perfect, i. e., it was still fluid at the end of the test (-22° F.).

The major portion of the product (150 g.) was extracted three times with 1500 cc. portions of acetone. The acetone solutions were combined and concentrated on the steam bath leaving a rather dark colored wax (100 g., Fraction 1). The acetone insoluble portion (50 g., Fraction 2) was a black tar. The latter contained the active pour depressant as indicated below for blends in the same oil as used above.

Pour point of blends, ° F.

	0%	¼%	½%	¾%	1%	3%	5%
Fraction 1.....	+30	---	+35	+30	+20	0	+10
Fraction 2.....	+30	-25	-25	-30	-30	---	---

A ½% blend of Fraction 2 was subjected to the standard S. O. D. test for pour stability. It showed a solid point at -20° F., i. e., it was not quite as good as the crude material in this respect.

The ratio of the dibasic acyl chloride, e. g., sebacyl chloride to the monobasic acyl chloride, such as stearoyl chloride, may be varied. It may be as low as 0.05 or may be increased to 0.5 or higher without impairing the oil solubility of the product. However, if this ratio is increased to above 0.8, an oil insoluble product results. The same holds true in general for the other acyl chlorides, bromides, and other halides.

It is not intended that this invention be limited by any of the examples which have been given merely for the sake of illustration, but only by the terms of the appended claims.

What is claimed is:

1. An improved non-volatile waxy hydrocarbon lubricating oil composition consisting essentially of a waxy mineral oil base stock and from 0.1 to 5.0% of a product obtained by heating a mixture of at least two different aliphatic carboxylic acid halides having from 10 to 30 carbon atoms per molecule at a temperature of 400° to 800° F. for a period of 1 to 20 hours.

2. A composition according to claim 1 in which at least one acid halide is a monobasic fatty acid halide and at least one is a dibasic fatty acid halide.

3. Composition according to claim 1 in which said halides are chlorides.

4. Composition according to claim 1 in which said halides are bromides.

5. An improved lubricating composition consisting essentially of a waxy mineral lubricating oil base and from 0.1% to 5.0% of a product obtained by heating a mixture of stearoyl halide and sebacyl halide wherein the ratio of the sebacyl halide to the stearoyl halide in said mixture is from 0.05 to 0.5 at a temperature of 500° to 700° F. for a period of 1 to 10 hours.

6. Composition as in claim 5 wherein said halides are chlorides.

7. An improved lubricating oil composition consisting essentially of a waxy lubricating oil base and from 0.1% to 0.5% of a product obtained by heating a mixture of stearoyl chloride and sebacyl chloride wherein the ratio of the sebacyl chloride to the stearoyl chloride in said mixture is from 0.05 to 0.5 at a temperature of 600° F. for a period of 6 hours.

8. An improved lubricating oil composition consisting essentially of a waxy lubricating oil base and a pour depressing amount of a product obtained by heating together a mixture of about 9 parts by weight of stearoyl chloride and about 1 part of sebacyl chloride at a temperature of 600° F. for a period of 6 hours.

9. An improved oil composition consisting essentially of a waxy mineral oil base of hydraulic oil to lubricating oil viscosity and 0.1 to 5% by weight, based on the weight of the oil, of the product obtained by reacting a monobasic acyl halide with a dibasic acyl halide at a temperature of 400° to 800° F. for a period of 1 to 20 hours.

10. A pour depressant composition for use in waxy oils and the like, consisting essentially of the reaction product of 0.5 to 8 parts by weight of dibasic acyl halide with 10 parts of monobasic acyl halide at a temperature within the range of 400° to 800° F. for 1 to 20 hours.

11. Composition as in claim 10 wherein the halides are chlorides.

12. Composition as in claim 10 wherein the dibasic acyl halide is sebacyl chloride and the monobasic acyl halide is stearoyl halide.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,033,546	Ralston et al.	Mar. 10, 1936
2,268,410	Lieber	Dec. 30, 1941